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PAPERS ACCEPTED FOR PUBLICATION:

The Determination of Methane, Carbon Monoxide, and Hydrogen by Explosion in Technical Gas Analysis. By W. A. Noyes and J. W. Shepherd.

On the Determination of Potash without the Previous Removal of Iron, Calcium, etc. By C. C. Moore.

Composition of the Ashes of Some Raw Tanning Materials. By Jno. H. Yocum.

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THE MOIST COMBUSTION METHOD OF DETERMINING CARBON IN STEEL.

BY GEORGE AUCHY.

Received February 9, 1898.

SOME recent experiences of the writer with the wet method of combustion show that this process may sometimes work faultily in the following particulars: First, the potash bulbs may not absorb all the carbon dioxide; Second, the "prolong" containing calcium chloride may not absorb all the moisture drawn over from the potash bulb; Third, the proportion of moisture so escaping from the prolong is not uniform and unvarying; Fourth, the potash solution may lose something besides moisture; Fifth, some chloro-chromic compound other than that absorbed by Prof. Langley's "pyro" mixture may occasionally form and cause high results.

With regard to the first of these points, it is the almost universal custom to use for the absorption of the carbon dioxide, a single set of weighed potash bulbs as directed by Blair in his description of the wet method. Prof. Langley, however, uses solid potash after the bulbs. Others use soda-lime tubes instead of potash bulbs. The writer in making determinations using the potash bulbs as customary obtained results varying very widely and was very much puzzled by them, believing at that time one set of bulbs to be ample for the complete absorption of the carbon dioxide. It was finally found, however, that a single set of bulbs is not always sufficient to absorb all the carbon dioxide in the wet method of combustion. Following are

the varying results spoken of, using but one set of potash bulbs.

	Per cent.		Per cent.
Steel 59 (Fresh potash)	1.97	Steel 1.00 standard	0.974
" 59	2.13	" 1.00 "	0.870
" 59	2.25	" 1.00 (Fresh potash)	0.890
" 59	2.07	" 35	0.333
" 59 (Fresh potash)	2.01	" 35	0.288
" 59	2.277	" 17	0.636
" 59 (Fresh potash)	2.18		

Two sets of potash bulbs were then employed with a calcium chloride prolong to each. After the second set of bulbs and prolong used, a weighed set of potash bulbs with the two anterior bulbs containing strong sulphuric acid was also used, the last bulb empty to avoid all danger of mechanical loss. Following this was the usual calcium chloride guard tube.

	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
Steel 59	2.267	none	2.267
" 59	2.280	none	2.280
" 1.00 standard	0.88	0.124	1.004
" 1.00 "	1.005	none	1.005
" 35	0.261	0.039	0.30
" 35	0.239	0.073	0.312
" 17	0.631	0.031	0.662
" 81	2.257	0.155	2.412
" 81	2.278	0.042	2.320[1]
" 81	2.115	0.285	2.400
" 80	3.145	0.070	3.215
" Tool	1.009	none	1.009
" 60	2.30	0.09	2.39
" *a*4	0.841	0.041	0.882
" *a*5	0.853	0.053	0.906
" *a*6	0.823	0.026	0.849
" 2*hh*	1.014	0.051	1.065
" 92	0.693	0.302	0.995
" 93	1.033	0.151	1.184
" 94	1.010	0.052	1.062
" 94	0.896	0.176	1.072
" 95	1.018	8.080	1.098
" 100	0.206	0.064	0.27
" 101	0.044	0.021	0.065
" 20	2.54	0.70	3.24

[1] This result is too low on account of incomplete solution of the steel by the double chloride solution.

The following were obtained by combustion with lead chromate and potassium dichromate:

	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
Steel 96	0.626	0.348	0.974
" 97	0.732	0.366	1.098

In all the above determinations the potash used was of specific gravity 1.27 as is customary and was frequently changed. In the following the strength of the potash solution was increased to 1.40 specific gravity. This latter strength was found much preferable, not only on account of the solution of that strength possessing greater absorbing power, but also because it can be used much longer in the potash bulbs without change:

Steel.	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
Tool, large	1.146	0.005	1.151
Tool, small	1.128	0.032	1.16
Nov. 13	1.14	none	1.14
Slab	1.103	0.015	1.118
E	1.042	none	1.042
T	1.023	none	1.023
Slab	1.09	0.02	1.11
106	1.379	none	1.379
No. 7	1.06	none	1.06
Cross cut	1.007	none	1.007
106	1.372	none	1.372
20	3.499	0.020	3.519
111 R	0.858	none	0.858
110	1.136	0.010	1.146
113	1.134	none	1.134
114	1.251	0.019	1.27
115	1.104	0.016	1.12
115	1.091	0.050	1.141
116	0.986	0.036	1.012
118	1.02	0.012	1.032
119	0.925	0.031	0.951
Trial	2.171	0.273	2.444
120	0.719	0.064	0.783
With fresh potash (sp. gr. 1.40).			
123	0.771	0.006	0.777
121	0.635	0.010	0.646
122	0.279	0.001	0.28
Shear	2.547	0.012	2.559

Steel.	Carbon in 1st set of bulbs. Per cent.	Carbon in 2nd set of bulbs. Per cent.	Total carbon. Per cent.
With new potash (sp. gr. 1.40).			
G	0.730	0.007	0.737
127	1.023	0.013	1.036
129	0.872	none	0.872
130	0.675	none	0.675
128	0.98	none	0.98
132	0.554	none	0.554
132	0.571	none	0.571
With fresh potash (sp. gr. 1.40).			
133	2.452	0.039	2.491
134	2.447	0.044	2.491
135	0.855	none	0.855
1.054 standard	1.033	0.030	1.063
136	0.906	0.023	0.929
137	1.301	none	1.301
With fresh potash (sp. gr. 1.40).			
138	1.298	none	1.298
139	0.98	none	0.98
138	1.27	none	1.27
1	1.167	none	1.167
2	1.122	none	1.122
3	1.101	none	1.101
4	0.957	0.008	0.965
5	1.116	none	1.116
With fresh potash (sp. gr. 1.40).			
6	0.959	none	0.989
*a*6	1.127	0.019	1.146
*a*1	0.984	none	0.994
*a*5	1.00	0.015	1.015
*a*3	1.052	none	1.052
Gin saw	0.89	none	0.89

The reason why one set of potash bulbs always suffices to absorb all the carbon dioxide in the dry combustion process,[1] and does not apparently always suffice in the wet combustion method, is doubtless that in the former way the evolution of the carbon dioxide is gradual and the gas largely diluted with oxygen, while in the wet combustion method the carbon dioxide is perhaps given off all at once in the beginning of the process, and hence in a state of greater purity and concentration. Results by the lead chromate method in the preceding table

[1] Dr. Drown, and doubtless many other chemists, by many experiments, has found this to be the case, and with the extensive use made of this method of combustion any tendency to loss in this manner could not have escaped notice.

indicate that when the carbon dioxide is given off almost pure and undiluted, the tendency of the gas to escape complete absorption by the potash bulbs is very great.

But in using potash of specific gravity 1.40, it is seen that the amount of carbon dioxide absorbed by the second set of bulbs is usually very small if any, and this small increase of weight is probably in very many cases not due to carbon dioxide but to moisture, for there is a certain quantity of moisture uniformly escaping absorption by the drying train. The drying train consists in this case of a Liebig bulb with strong sulphuric acid, then a large U-tube filled with calcium chloride followed by potash bulbs with strong sulphuric acid. The unabsorbed moisture is consequently caught, or partly caught, by the absorption apparatus, and constitutes almost, if not quite, the entire "dummy" to be deducted from the result in an ordinary determination. And the amount of the moisture so escaping the drying train, and absorbed, or partly absorbed, by the two sets of potash bulbs and prolongs, although pretty uniform and unvarying in total amount as shown by blank tests, is nevertheless varying as regards the proportion absorbed by each absorption set. Results are shown by the following tests made in blank, with the same amount of reagents, etc., as in a regular test.

	First set of bulbs and prolong. Equivalent to carbon. Per cent.	Second set of bulbs and prolong.[1] Equivalent to carbon. Per cent.	Total moisture equivalent to carbon. Per cent.
One-half hour's aspiration	0.015	0.060	0.075
" " "	0.051	0.016	0.067
" " "	0.060	0.019	0.079
" " "	0.056	0.015	0.071
" " "	0.076	0.005	0.081
" " "	0.055	0.013	0.068
" " "	0.061	0.020	0.081
" " "	0.055	0.026	0.081
" " "	0.030	0.028	0.058
" " "	0.041	0.031	0.072
One-fourth hour's aspiration	0.041	0.028	0.069
" " "	0.049	0.020	0.069
" " "	0.019	0.046	0.065
" " "	0.024	0.040	0.064
" " "	0.036	0.028	0.064
" " "	0.035	0.024	0.059

[1] Also weighed strong sulphuric acid bulb to this set.

Fresh sulphuric acid in drying train.

	First set of bulbs and prolong. Equivalent to carbon. Per cent.	Second set of bulbs and prolong.[1] Equivalent to carbon. Per cent.	Total moisture equivalent to carbon. Per cent.
One-fourth hour's aspiration	0.047	—0.006	0.041
" " "	0.052	0.016	0.062
" " "	0.048	0.019	0.067
" " "	0.039	0.021	0.060
" " "	0.000	0.057	0.057

That these gains in weight are due mainly if not quite to moisture that the drying train failed to absorb, is shown by the following tests in which purified air was simply aspirated through the apparatus for about the same length of time, and as nearly as possible at the same rate of speed as the gas is evolved and air aspirated in an ordinary test.

	First set.	Second set.	Total moisture.
One-half hour's aspiration	0.058	0.000	0.058
One-fourth " "	0.038	0.026	0.064
" " "	0.032	0.044	0.076
Five minutes' aspiration	0.012	0.033	0.045

It is seen that there may be, in different determinations, considerable variation in the proportion of moisture absorbed by each set of bulbs, although the total amount is usually 0.065 per cent. in terms of carbon, or quite close to it. So in deducting "dummies" from each set of bulbs, this variation may cause an absorption of carbon dioxide to be indicated by the second set of bulbs, when in reality the gain in weight of this set of bulbs may be due merely to a variation in moisture from the "dummy" subtracted. The results with use of potash of 1.40 specific gravity therefore do not prove, when the amount of carbon is not unusually large, and the potash solution not too long in use, that one set of bulbs, using potash of that strength, is insufficient. These results, and the dummy results following, indicate very plainly, however, the necessity for using more than one drying apparatus after and with the potash bulbs. Mr. David H. Browne, in his admirable "Hints to Beginners" in *Journal of Anal. and Appl. Chem.*, speaks of this in connection with the wet method, although the necessity of it is perhaps not generally recognized. But there is some little difference of opinion among chemists who use the other (dry) method of combustion;

[1] Also weighed strong sulphuric acid bulb to this set.

Dr. Drown, for instance, has found a single prolong filled with calcium chloride sufficient to catch all the moisture from the potash bulbs. On the other hand Mr. Andrew A. Blair has noticed a loss of moisture from the prolong; and Dr. Dudley also hints at the same thing, and thinks it probable that "some of the difficulty in getting absolute blanks may be accounted for in this way." It is not strange that in the dry method with a careful performance of the operation there should be, with some manipulators, a complete absorption of the moisture by the prolong. But in the wet method where the evolution of gas is more abundant and longer continued, it is the writer's experience, at least, that the prolong filled with freshly dried calcium chloride usually falls very short of absorbing all the moisture from the potash bulbs, the moisture thus lost amounting sometimes to as high as 0.14 per cent. in terms of carbon with one-half hour's aspiration.

But the escape of moisture from the prolong would be of no serious consequence (if dummy tests were carefully made) provided the moisture so escaping was invariably uniform in amount. The following tests, however, show a very great lack of uniformity in this respect and illustrate the necessity, in the wet method, of having more than the usual drying agencies after the potash bulbs to insure a uniform though probably still not complete absorption of the moisture from the potash bulbs. In these tests the moisture lost from the prolong was determined by absorbing it in a weighed potash bulb following and connected with the prolong, and having the two anterior bulbs filled with strong sulphuric acid. The results are consecutive, and are expressed in terms of carbon per cent:

One-fourth hour's aspiration—equivalent to carbon, per cent.: minus 0.005 per cent.; plus 0.004 per cent.; 0.004 per cent.; 0.004 per cent.; 0.002 per cent.; 0.015 per cent.; 0.008 per cent.; 0.010 per cent.; 0.019 per cent.; 0.017 per cent.; 0.013 per cent.; 0.023 per cent.; 0.021 per cent.; 0.026 per cent.; 0.021 per cent.; 0.048 per cent.; 0.062 per cent.; 0.060 per cent.; 0.062 per cent.; 0.058 per cent.; 0.060 per cent.; 0.052 per cent.

With fresh calcium chloride in prolong: 0.015 per cent.; 0.003 per cent.; 0.018 per cent.; 0.012 per cent.; 0.015 per cent.; 0.000 per cent.; 0.018 per cent.; 0.015 per cent.; 0.010 per cent.; 0.009 per cent.

With fresh calcium chloride, and one-half hour's aspiration: minus 0.006 per cent.; 0.005 per cent.; 0.015 per cent.; 0.023 per cent.; 0.018 per cent.; 0.018 per cent.; 0.012 per cent.; 0.018 per cent.; 0.027 per cent.; 0.032 per cent.; 0.010 per cent.; 0.006 per cent.; 0.016 per cent.; 0.012 per

cent.; 0.020 per cent.; 0.025 per cent.; 0.022 per cent.; 0.016 per cent.; 0.022 per cent.; 0.028 per cent.; 0.044 per cent.; 0.049 per cent.; 0.076 per cent.; 0.077 per cent.; 0.071 per cent.; 0.055 per cent.; 0.046 per cent.; 0.053 per cent.; 0.119 per cent.; 0.138 per cent.; 0.074 per cent.; 0.081 per cent.; 0.065 per cent.; 0.053 per cent. Then with one-fourth hour's aspiration 0.043 per cent.; 0.052 per cent.; 0.050 per cent.; 0.042 per cent.; 0.081 per cent.; 0.050 per cent.; 0.043 per cent.; 0.043 per cent.; 0.046 per cent.; 0.029 per cent.

The sulphuric acid bulbs in their turn doubtless let some moisture through; but that by their use in connection with the prolong uniformity is obtained, is shown by the dummy results already given.

It is not supposed that the prolong and the sulphuric acid bulbs together absorb absolutely all the moisture from the potash bulbs for the reason that the drying train before the potash bulbs, consisting of two sulphuric acid bulbs, and one large calcium chloride tube, allows moisture equivalent to 0.065 per cent. carbon to escape in the course of a determination and therefore the drying apparatus after the potash bulbs doubtless also allows moisture to escape.

The writer is inclined to think that no apparatus now used in the absorption of moisture in the carbon process will absorb the moisture completely when the flow of gas is brisk and continued as in the wet method. Mr. A. A. Blair considers anhydrous copper sulphate an excellent absorbent of moisture. In fact it dries the gas too thoroughly; so that, as Mr. Blair says, "the gas leaves the prolong with more moisture than when it entered the absorbing apparatus." He therefore places a plug of moist cotton wool after the copper sulphate in the drying train and before the calcium chloride tube of the drying train in order to secure a uniformity of conditions in this particular. The loss of moisture from the prolong is thus equalized by a gain of moisture from the calcium chloride tube of the drying train. In this connection it is interesting to note a difference of opinion between Mr. Blair and Dr. Drown and others. Dr. Drown says that he finds no advantage in the use of the plug of moist cotton wool. Mr. Shimer, Dr. Dudley, and others seem to find no occasion for its use. As the only difference between the apparatus of Messrs. Drown, Dudley, and Shimer on the one hand, and Mr. Blair on the other (excepting the preheating furnace), is that the

former contains ferrous sulphate solution in the train immediately preceding the copper sulphate tube, it would seem a plausible inference that in the former case a plug of moist cotton wool, before the calcium chloride train is not needed because the moisture from the ferrous sulphate solution supplies the amount necessary to counterbalance that lost from the prolong—the anhydrous copper sulphate intervening in Messrs. Drown and Shimer's apparatus being in that case not so good a drying agent after all.

However easy and tempting this deduction may be, it is nevertheless inadmissible from the simple fact that Dr. Drown finds that no moisture at all escapes from the prolong in his use of it. Hence the only explanation left us for the fact that Mr. Blair finds the use of moist cotton wool necessary or advisable and Messrs. Drown, Dudley, and Shimer do not, is of course the simple one that in the one case the passage of gas and the aspiration of air is allowed to proceed more gently than in the other, so that in this case moisture is neither drawn from the drying train on the one hand, nor lost from the prolong on the other. This is of course a perfectly reasonable supposition, but if a difference in manipulation merely (and probably a slight difference) is responsible for this difference in behavior, then it would seem best for the ordinary operator to be on the safe side by assuming that moisture does escape from the prolong, and to proceed accordingly.

The writer nevertheless ventures to question whether there is any real need of introducing the moist cotton wool into the apparatus—whether, in fact, it is not distinctly inadvisable so to do. For, the less moisture carried into the weighed absorbing apparatus, the less variable will obviously be the amount of moisture escaping from it and the less, therefore, "the difficulty of obtaining absolute blanks," and the more concordant the results. If more moisture escapes absorption by the prolong than is gained from the drying train, and the dummy is therefore a minus quantity, so much the better, showing, as it does, that the drying train is a good one and allows but little moisture through it. And it is just as easy to apply a plus correction to the result in a regular determination as a minus one; that is, if our dummy is minus we add instead of subtracting it from our results. The important matter is, of course, to get an absolute

dummy—one that does not vary, and the writer therefore thinks it better still to use a weighed sulphuric acid bulb or some other additional drying apparatus after the prolong to secure this uniformity until convinced by many such trials that (in the operator's manner of procedure) no moisture escapes absorption by the prolong. For the writer, moisture does escape from the prolong, in the dry as well as in the wet method of combustion, varying in the dry method from 0.000 per cent. to 0.08 per cent. in terms of carbon, according to the freshness of the calcium chloride, its state of division, and the speed of aspiration. In using calcium chloride Dr. Dudley directs that it be freshly dried before use. This is such a necessary precaution as to bear much iteration.

A calcium chloride tube filled directly from a half-emptied bottle and therefore without previous drying lost by aspirating dry air through for two hours, equivalent to carbon: 0.047 per cent.; repeated, lost 0.14 per cent.; again, gained 0.02 per cent.; again, lost 0.19 per cent.; again, lost 0.48 per cent.

A wash-bottle with water was followed by this calcium chloride, and that in its turn by a weighed sulphuric acid bulb. The bulb gained in weight 0.32 per cent. and 0.29 per cent., so that the drying of the calcium chloride previous to use is an absolutely necessary precaution.

It seems to be necessary with some potash solutions to aspirate air through before using. Several blank tests made without doing this showed a loss of weight, in the one case equal to 0.048 per cent. carbon and in the other 0.019 per cent. carbon.

In the writer's experience a most serious difficulty with the wet method of combustion is, that occasionally results are obtained from 0.05 to 0.07 per cent. above the truth, due apparently to some chloro-chromic compound other than that absorbable by Prof. Langley's "pyro" mixture. At least the writer can offer no other explanation, the purifying train including: water kept cold for hydrochloric acid according to Porter Shimer; ferrous sulphate for chlorine according to Dr. Dudley; "pyro" mixture for chlorine, oxides of chlorine, and chloro-chromic anhydride according to Prof. Langley; and silver sulphate in strong sulphuric acid for hydrochloric acid.

It is known that the wet method is unsuited for graphite de-

terminations owing to a portion of the graphite being oxidized merely to carbon monoxide.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S. DEPARTMENT OF AGRICULTURE, No. 30.]

COMPARISON OF THE STANDARD METHODS FOR THE ESTIMATION OF STARCH.[1]

BY H. W. WILEY AND W. H. KRUG.

Received February 15, 1898.

THE study of the nature of the carbohydrate bodies which exist in foods has been vigorously prosecuted by chemists in different parts of the world during the past few years. The result of these studies has been to arouse new interest in the standard methods of starch determination. The numbers which are secured by different workers for starches vary so greatly as to lead to the belief that the estimation of starch is not such an easy matter as is generally supposed; in fact, long experience has convinced us that there are few operations in agricultural analytical chemistry which require greater skill, or are attended with greater difficulties than the estimation of starch in the presence of the other carbohydrate bodies.

At a recent meeting of chemists in England, it was stated in one of the papers that the methods of starch determination are now so easy of application and so accurate that there is no longer any excuse for being ignorant of the exact content of starch in any body. Stone, in Bulletin No. 34 of the Office of Experiment Stations, described a method which was easily seen to be erroneous, yielding only about half as much starch as was really contained in the samples examined. A cursory glance at the methods of analysis employed by him convinced us that the fault was insufficient saccharification, due to the weakness of the acid and the shortness of the time of heating.

In a subsequent article[2] Stone called attention to the error of his previous statements, and proposed a modification of his first published method, which, as is seen below, gives very much better results. Having to estimate, annually, the starches in many hundreds of substances, we were led to make a compara-

[1] Read before the American Chemical Society and Section C of the American Association for the Advancement of Science, at Detroit, August 12, 1897.

[2] This Journal, 19, 347.

tive study of the standard methods which have been used for starch determination, and of some modifications which seemed to us worthy of trial. The standard methods which we employed were those described in "Principles and Practice of Agricultural Analysis," 3, 196–222, and 300–302. The materials which we used in our investigations were starches of commerce, the ordinary cereal grains, and a sample of the wheat which was the subject of the investigations of Stone, and which was kindly furnished us by Professor Stone. We give below a brief résumé of the work we have done.

The sample of spring wheat No. 1, which we received from Professor Stone, was examined for all of its principal constituents, according to the official and standard methods of analysis, and the data obtained by him and by us are given below. The moisture stated in the second column of the appended table was determined by drying for five hours in a high vacuum at 100°.

PRELIMINARY GENERAL ANALYSIS.

Spring wheat No. 1.	Data obtained by Stone. Per cent.	Wiley and Krug. Per cent.
Moisture	8.55	10.65
Ether extract	2.00	2.24
Ash	1.43	1.77
Fiber	2.77	2.56
Albuminoids	14.22	14.44
Pentosans	4.54	5.17
Starch and undetermined	66.49	63.17

Before determining the starch it seemed of interest to take the sample in the state in which it was sent, as we assumed that it had thus been analyzed by Professor Stone. It also seemed to us that the digestion with malt extract prescribed by him was not long enough to insure the complete conversion of the starch into maltose and dextrins. To determine this, one set of samples was digested one hour at 60°, and another set two and one-half hours at 50°, since Lintner states that diastase is most active at this latter temperature. The results obtained show that our surmise was correct.

Spring wheat No. 1.	Stone method. Per cent. of starch.	Wiley and Krug method. Per cent. of starch.
a	56.27	57.39
b	57.00	58.73
c	58.65	59.88
Means	57.31	58.66

The residues from the diastase digestion were all thoroughly washed with hot water and then examined with iodine under the microscope. In every case a large number of cells was found which contained undigested starch, showing that the sample had not been ground to a sufficient degree of fineness. This is, therefore, another source of error in Professor Stone's work. The sample was then reground and the starch determined by three methods; *viz.*, first, the Reinke lactic acid method, second, a method which differs from this by the use of five-tenths gram of salicylic acid instead of lactic acid, and third, the diastase method. The residues were again examined and in every case found free from starch, showing that the conversion had been complete.

The following results were obtained:

Spring wheat No. 1.	Reinke method. Per cent. of starch.	Salicylic acid method. Per cent. of starch.	Diastase method. Per cent. of starch.
a	62.22	63.25	62.66
b	62.41	63.09	62.25
c	....	62.94	....
Means	62.32	63.09	62.46

As is subsequently shown, the result obtained by the last method is more probably correct. The number for starch thus obtained, added to our per cents. of the other constituents gives us a total of 99.28. The separate determination of the sucrose, galactan, invert sugar, and dextrin, originally present, was omitted, and these bodies are included with the starch.

This work led us to undertake an investigation of other methods for the determination of starch which have been proposed from time to time, our desire being to avoid, if possible, the use of diastase and to shorten the time of procedure.

It seemed that this might be accomplished by polarizing the

products of hydrolysis and thus avoiding the labor incident to the gravimetric method of determining copper. To this end, several methods were tried. These methods depend either on the complete conversion of the starch into dextrose or on the formation of soluble starch, maltose, and dextrins.

THE GUICHARD METHOD.

Guichard[1] proposes to boil four grams of the material for one hour with 100 cc. of ten per cent. nitric acid (ten cc. strong acid (sp. gr. 1.42) to ninety cc. water) in a flask provided with a return condenser. The solution is cooled, filtered, and polarized. The starch is found by the formula

$$A = \frac{av \times 25 \times 0.016}{2 \times 52.8},$$

where a = rotation in angular degrees, v = volume of liquid, and A = starch transformed. As our polarizations were made with a Schmidt and Haensch instrument, the dextrose was determined by the formula

$$(a)_D = \frac{a \times 100}{c \times 1},$$

where a = rotation, c = weight of dextrose, l = length of tube in dm., and $(a)_D = 52.8°$.

THE PRESSURE METHOD.

Three grams of substance are heated in a flask with eighty to ninety cc. of water until pasty, and the starch rendered soluble by heating from three to five hours in an autoclave, at from two to three atmospheres. The volume is completed to 100 cc. and the solution polarized. The gyrodynat of soluble starch prepared in this way varies from $(a)_D = 196.5°$ to $197°$.

THE BAUDRY METHOD.

To 2.883 grams of the substance (for Schmidt and Haensch instrument) add from eighty to ninety cc. of water and five-tenths gram salicylic acid. Boil twenty minutes, dilute to about 190 cc., add one cc. ammonia, cool, dilute to 200 cc., filter, and polarize in a 400 mm. tube. Multiply the result by three. Baudry determined the gyrodynat of soluble starch to be $(a)_D =$

[1] This and the following polarimetric methods are described in detail in Vol. III of "Principles and Practice of Agricultural Analysis."

202.66° at 15°–18° C., when sucrose = 67.3° (Girard and de Lugnes), and 200.25° when sucrose = 66.5° (Tollens). As the normal weight for sugar is 26.048 grams ($(a)_D = 66.5°$) the normal weight for starch will be $\frac{26.048 \times 66.5^{\circ}}{200.25^{\circ}} = 8.650$ grams.

We furthermore tried to apply polarization to the solution obtained by the Reinke method. Three grams of the material were heated two and one-half hours in the autoclave with thirty cc. of one per cent. lactic acid and 25 cc. of water at three and one-half atmospheres, diluted to about eighty cc. and inverted two and one-half hours with five cc. hydrochloric acid of 1.20 specific gravity. The volume of the solution was then completed to 100 cc., filtered, and polarized. The results show that the polarizing power of the solution was too high and that too little acid had been used, and another series was made in which the quantity of acid was doubled. In this case, the results were too low. The solutions were always highly colored, and we were unable to polarize them without previous treatment with bone-black. In the following table are given the results obtained by the polarimetric methods above described.

Nos. 1 and 2 are samples of commercial corn starches, Nos. 3 and 4 specimens of wheat obtained at the Columbian Exposition.

COMPARISON OF POLARIMETRIC METHODS ON STARCH AND WHEAT.

	Guichard method. Per cent. starch.	Pressure method. Per cent. starch.	Baudry method. Per cent. starch.	Reinke method. Five cc. acid. Per cent. starch.	Reinke method. Ten cc. acid Per cent. starch.
1. Starch	81.9	....	67.8	100.16	76.33
	80.04	....	....	101.26	76.33
	80.96	....	....	....	....
Means..	80.97	....	....	100.71	76.33
2. Starch	83.72	....	80.4	101.81	79.73
	84.18	....	....	102.90	76.33
Means..	83.95	....	....	102.36	78.03
3. Wheat	55.43	36.45	28.89	83.45	50.35
	55.94	41.66	....	82.26	49.86
Means..	55.69	39.06	....	82.66	50.11
4. Wheat	53.59	36.45	36.00	96.56	49.62
	53.13	36.45	35.46	92.99	49.34
Means..	53.36	36.45	35.73	94.78	49.48

This table shows that there is much variation between the results obtained by the different methods. The Guichard method gives promise of being applicable to pure starches, but does not give good results with wheat. When the nitric acid is added to the cereal the oxidizing action is very violent for some minutes, and the proteid matters which are brought into solution doubtless counteract, to some extent, the right-handed rotation due to the dextrose formed. It is evident also that the acid brings a large proportion of the pentosans into solution. It seems probable that a careful study of the conditions under which the Reinke method should be used may render this method available. The pressure method fails to render all the starch soluble, as was shown in the work with pure starch, where in every case the solution contained large quantities of gelatinized starch, which made filtration and polarization almost impossible.

The use of salicylic acid in the Baudry method suggested its substitution for lactic acid in the Reinke method, as it was noticed that the solutions obtained with it were very free from caramelization. It was found that this was also true of the solutions obtained with it in the autoclave. The results were proportionately higher and indicate that lactic acid in conjunction with the pressure decomposes a considerable portion of the pentosans present. Comparative estimations on the same samples gave the following results:

Material.		Lactic acid. Per cent. starch.	Salicylic acid. Per cent. starch.
1. Starch		82.93	84.27
2. Starch		82.60	84.03
3. Cornstarch	*a*	83.96	*a* 84.27
	b	83.66	*b* 84.46
	c	83.84	*c* 84.21
	d	83.72	*d* 84.24
Means		83.795	84.295
4. Wheat		62.25	63.17
5. Wheat		62.32	63.09

These figures show a fairly uniform increase in the amount of starch found when salicylic acid was used. It might be claimed that this increase in the case of wheat is due to the greater solubility of the pentosans present in the cereal and not to the greater solvent power of the salicylic acid on starch. In order

to determine whether this is the case, three grams of wheat were treated in the autoclave by two methods, 100 cc. of the filtrate distilled with twelve per cent. hydrochloric acid and the furfurol determined. It was found that lactic acid dissolved 3.55 per cent. of pentosans and salicylic acid 3.69 per cent. in terms of the substance. It is therefore evident that both acids exert a like hydrolyzing power on the pentosans and the increased percentage of starch by salicylic acid is not due to this property. The solutions obtained with salicylic acid were never at any stage of the process darker than a straw-yellow while the final liquid obtained with the Reinke method is generally deep brown, showing that considerable caramelization has taken place. We therefore recommend the use of salicylic acid in place of lactic acid when it is necessary to determine the fermentable constituents of a cereal by the high pressure method, and also with the proper corrections for general analytical work.

METHOD OF LINDET.

Lindet[1] describes the following method for the direct determination of starch.

According to an observation of Girard, the grains of starch in the cereals are surrounded with a glutinous envelope, and the principle of the new process of Lindet is based upon the solution of this envelope by pepsin under such conditions as to prevent any hydrolysis of the starch. After the solution is complete, the starch granules are easily washed out, collected, dried, and weighed. The process is therefore one for the direct determination of starch, and gives promise of usefulness in the technical examination of cereal grains to be used for starch-making. The cereal grains are finely ground and ten grams of the flour are placed in a vessel and covered with a solution containing two per cent. of pepsin and one and one half per cent. of hydrochloric acid. The mixture is left for twelve or fourteen hours, with frequent shaking, at a temperature of from 40° to 50°. The contents of the vessel are then poured upon a fine bolting-cloth, the cloth gathered into the form of a knot and washed in a capsule of water until starch is no longer removed. The wash-waters containing the starch are brought together, treated with

[1] Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie, 14. 405

a little formic aldehyde or mercuric chloride to prevent bacterial action, and the starch is collected upon a weighed filter. The filtration is somewhat tedious, especially when the cereal contains large quantities of gum. It can be facilitated, to a certain degree, by adding to the filter a known quantity of calcined and washed pumice stone. The collected starch is dried at first at 50° and finally at 150°. Lindet has assured himself, by careful trial, that the presence of the hydrochloric acid in the quantity noted above prevents the action of any of the natural diastases or enzymes which the cereal may contain upon the starch, but that a hydrochloric acid of that strength exercises, at the temperature employed, no hydrolyzing effect whatever upon the starch granules.

The method appeared to be so short and easy of manipulation that we decided to try it. For this purpose four cereals were purchased and prepared; *viz.*, wheat, oats, rye, and barley. A general analysis was first made which gave these results:

	Wheat. Per cent.	Rye. Per cent.	Oats. Per cent.	Barley. Per cent.
Moisture	11.33	11.71	9.26	12.20
Ether extract	2.00	1.63	4.72	0.92
Fiber	2.15	2.36	12.81	0.80
Ash	1.69	2.31	3.78	0.93
Proteids	12.19	11.69	9.63	10.44
Pentosans	5.80	8.10	13.65	6.50
(*a*) Starch[1] (salicylic acid method)	64.41	62.64	46.78	68.38
(*b*) Starch[1] (diastase method)	63.17	61.55	45.05	67.56
Total (including starch *a*)	99.57	100.44	100.63	100.17
Total (including starch *b*)	98.33	99.35	98.90	99.35

The starch was determined both by the use of salicylic acid as described above and by the means of diastase. The increase due to the hydrolyzing action of the acid is clearly shown by the data and proves that its use as well as that of other organic acids is warranted only when analytical data are desired in connection with the technical use of high pressure in commercial operations, or when the final data are corrected as hereinafter described.

[1] Including sugar, galactan, dextrin, etc.

In our application of the Lindet method to these cereals we reduced the amount taken to three grams, as it seemed desirable to estimate the starch not only by direct weighing but also after conversion into dextrose, and this quantity was found very convenient to handle on the bolting-cloth. The starch was also determined in the residue left on the cloth, and the starch which was washed through was dried and weighed, then gelatinized, treated with malt extract, and determined as usual. It was then found that in most cases some fiber had gone through the cloth and rendered the results too high.

LINDET METHOD.

	Direct weight.			Determination after conversion into dextrose.			
Cereal.	Starch. Per cent.	Residue. Per cent.	Total. Per cent.	Starch. Per cent.	Residue. Per cent.	Total. Per cent.	Fiber in starch. Per cent.
Oats	44.19	0.14	44.33	44.27	0.14	44.41	....
	44.31	0.00	44.31	43.73	0.00	43.73	0.58
	43.81	0.33	44.14	43.47	0.32	43.80	0.34
Barley ...	71.41	0.97	72.38	66.47	0.97	67.44	4.94
	72.72	0.00	72.72	67.47	0.00	67.47	5.25
	71.66	0.98	72.64	66.51	0.98	67.49	5.15
Rye.....	61.24	0.79	62.03	58.18	0.79	58.97	3.06
	60.83	1.21	62.04	57.94	1.21	59.15	2.89
	59.83	2.41	62.24	57.68	2.41	60.09	2.15
Wheat ...	67.35	0.00	67.35	60.18	0.00	60.18	7.17
	66.05	0.60	66.65	60.11	0.60	60.71	5.94
	66.55	0.00	66.55	60.26	0.00	60.26	6.29

This table shows that not quite all the starch was removed by the washing in every case, and that some material which is not starch is counted as such. It required almost a week to filter the liquid containing the starch and this was no doubt due to the pepsin present. It was also quite impossible to keep some of the starch granules from running through the filter. The method is therefore more tedious than the common processes and not nearly so accurate.

One of the main sources of error in the estimation of starch in a cereal is the difficulty of converting it all into soluble products. This is due to the fact that the starch granules are imbedded in proteid matters and are thereby partially protected from the action of the solvent. We have therefore combined the use of pepsin to dissolve this protein with the salicylic acid method

described above. Three grams of the cereal were digested fourteen hours at 45° C. with thirty cc. of pepsin solution, the hydrochloric acid carefully neutralized with sodium carbonate, five-tenths gram salicylic acid added, and the material heated two and one-half hours in the autoclave to three and one-half atmospheres. The neutralization of the hydrochloric acid is necessary, since it would dissolve additional quantities of the pentosans present. Some curious color-reactions took place during the process. The neutralization with sodium carbonate turned the solution light green. On removal from the autoclave it was found to be a straw-yellow, but after neutralizing the hydrochloric acid used in the final inversion the liquid again became deep green. This is probably due to the products formed by the action of the pepsin on the proteids. The results obtained follow:

	Starch.			Means.
	Per cent.	Per cent.	Per cent.	Per cent.
Wheat	64.50	64.51	64.44	64.48
Rye	62.41	62.14	62.50	62.35
Oats	47.29	47.42	47.08	47.26

A comparison of these results with those obtained by the salicylic acid method alone shows a close concordance. The use of pepsin is, however, a safeguard which it is well always to apply as it insures the thorough solution of the starch. The pepsin must be free from material which exercises a reducing action on the copper solution. We have also tried the combination of the pepsin and diastase digestions, but reserve the report on this method for further study.

We also have thought it advisable to apply taka-diastase instead of malt extract for dissolving the starch, since it can easily be obtained in a dry form and retains its activity for a considerable length of time. We were not able to study its action thoroughly on account of lack of time, but found that five-tenths gram of taka-diastase required twelve hours to completely dissolve the starch in three grams of wheat. The experiment was made at 50°. It was found that the taka-diastase contained no reducing substances, which is an advantage over malt extract. The solutions obtained with it had commenced to decompose at

the end of twelve hours and it was therefore deemed inadvisable to estimate the starch in them.

We have also tried quite extensively the pancreatic diastase prepared by Frederick Stearns & Co., of Detroit, and found it exceedingly active and free of any reducing matter. The indications are that it may prove to be the most desirable form of hydrolyzer yet used. The data obtained by us with this reagent will be increased and made the subject of another communication.

Following are the conclusions which are drawn from the vast amount of analytical data which has been accumulated.[1]

1. All the heretofore described methods for determining the percentage of starch by polarization, whether with the soluble starch or with dextrose made therefrom, are liable to grave errors and none of them can be relied upon to give accurate results. The only advantage which can be claimed for such methods is in the saving of time. The sources of error, however, are so great as to nullify the advantage of time-saving.

2. The methods depending upon hydrolysis in an atmosphere of steam under pressure are obnoxious to the danger of caramelization. This seems to be entirely prevented by the addition of a very small quantity of an organic acid. Of the organic acids suggested tartaric is excluded on account of its optical properties. Of lactic and salicylic acid the latter is to be preferred. In all cases where dilute organic acids are employed the pentosans of the cereal and its products are hydrolyzed to a considerable extent. The presence of the sugars produced by the hydrolysis of the pentosans increases the quantity of metallic copper obtained and thus raises the apparent percentage of starch. In these cases, a correction must be made by determining the quantity of pentose sugar present and diminishing the percentage of starch obtained in proportion to the quantity of pentose sugar found.

In this instance, a difficulty arises from the uncertainty concerning the quantity of pentosan corresponding to a given amount of sugar produced therefrom reckoned as dextrose. We have seen

[1] More than 500 gravimetric determinations have been made by Mr. W. H. Krug in prosecuting this research. In each case the reduced cuprous oxide was dissolved and the metallic copper precipitated electrolytically.

that salicylic acid, in the autoclave, under the conditions specified above, dissolved 3.69 per cent. of pentosans calculated on the weight of the ground cereal employed. We have shown in another paper that diastase dissolves very little pentosan from cereals. It is therefore easy to make a determination of the copper reducing power of the dissolved pentosans reckoned in terms of dextrose. In a preceding table, we have shown the excess of reducing sugar, obtained by the salicylic acid under pressure, over the amount secured by the diastase method without pressure. In the case of wheat this excess was 1.24 per cent., in rye 1.09 per cent., in oats 1.73 per cent., and in barley 0.82 per cent.

The mean excess for the four cereals examined was 1.23 per cent. In the case of wheat, therefore, it is seen that 3.69 per cent of dissolved pentosans yielded an amount of reducing sugar equivalent to only 1.24 per cent. of dextrose. We therefore propose, in the case of wheat, when the salicylic acid method is used with pressure in the autoclave, to diminish the apparent per cent. of starch by 1.25. . Where greater exactitude is required the pentosans should be determined and the per cent. found divided by three. The quotient will be the figure to be subtracted from the apparent percentage of starch obtained.

3. The direct weighing of the starch, according to the method of Lindet, after solution of the protein by means of pepsin, has many advantages for practical work, especially in starch factories. Small particles of other matters, however, of no greater size than the starch grains themselves, pass through the bolting-cloths and are reckoned as starch in the final weighings. This error is partly compensated for by a portion of the starch remaining attached to the filter and the final result by the Lindet method is in some cases approximately correct.

4. The combination of the Lindet method, in so far as the solution of the protein is concerned, with the diastase method as practiced by us, has given most encouraging results and it is probable that a satisfactory method of starch estimation can be worked out in this line.

5. The diastase method without pressure gives satisfactory results when the diastase is freshly prepared and used in proper quantities and at an appropriate temperature. The diastase

exerts only a small solvent action on the pentosans and the final hydrolytic products obtained are not contaminated with any appreciable amounts of pentose sugars. The use of taka-diastase is worthy of further investigation since it can be easily prepared uncontaminated with any reducing sugars. The sample we employed, however, was not very active, requiring several hours more time for a complete solution of the starch than diastase recently prepared from malt. The materials on which the diastase acts should be ground to the finest possible powder and should be previously extracted with ether to prevent the retarding action of fat on the ferment. The treatment with diastase should always be repeated after boiling and cooling to about 50°. The residue must not show any starch granules when stained under the microscope with iodine.

6. The time at our disposal did not permit us to make a comparative trial of saliva as a solvent for the starch. This part of the problem remains to be worked out, and it is hoped that saliva will be found to exert a minimum solvent action on the pentosans and celluloses present in cereals.

7. The summation of the several per cents., obtained in the analysis of a cereal or cereal product by the methods employed by us, does not in all cases approximate closely to 100. The variations are somewhat greater than in ordinary mineral analysis. They are, however, not of such a magnitude as to warrant the assumption of the existence in cereals of a class of bodies of unknown properties and different in any marked degree from those already known to exist. In this connection, it should not be forgotten that in the estimation of the ash by the official method there is danger of loss of chlorine, sulphur, and phosphorus, especially of the former and latter, the organic phosphorus escaping combination with the already saturated bases present. In some recent experiments we have found the loss to be more than one per cent. of the total weight of the cereal employed. When this fact is taken into consideration, it is evident that there is practically no constituent unaccounted for in the analytical data. The small quantity of matter unaccounted for in the cereal grains is doubtless of a carbohydrate nature, belonging to that complex class, pentosan-ligno-celluloses, whose chemical and physical properties are so nearly alike as to make

their exact separation and determination extremely difficult. The quantity of these undetermined bodies in cereal grains is very minute. In stalks and straw, and other bodies containing a large excess of ligno-cellulose compounds, this quantity is doubtless much larger.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE U. S DEPARTMENT OF AGRICULTURE, No. 31.]

THE SOLUBILITY OF THE PENTOSANS IN THE REAGENTS EMPLOYED IN THE ESTIMATION OF STARCH.

BY W. H. KRUG AND H. W. WILEY.[1]

Received February 15, 1898.

THE methods which have been generally adopted for the quantitative determination of starch in a cereal or fodder are based on one or two principles; *viz.*, the application of high pressure in contact with water containing some organic acid, to prevent the decomposition of the sugars formed during the hydrolysis, or the conversion of the starch by means of diastase. The results obtained by the former methods are always a little too high and do not represent the actual starch content of the material under examination. In analytical work where it is desired to obtain the exact percentage of starch, diastase must be used and the application of any acid avoided until those bodies which may be acted upon by it have been removed by filtration, or else a correction must be applied as described in our preceding paper. The increased amount of starch found by the use of high pressure methods is due to the action of the organic acid on the pentosans and hemicelluloses present which results in the formation of reducing substances.

We have determined the amount of pentosans dissolved in the application of these methods with the following results:

1. Solubility of the pentosans by digesting for two and one-half hours at three and one-half atmospheres with thirty cc. of water and twenty-five cc. of one per cent. lactic acid:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved. In per cent. of substance.	Pentosans dissolved. In per cent. of pentosans.
Wheat No. 1	5.80	4.63	79.83
Wheat No. 2	5.17	4.66	90.13

[1] Read before the American Chemical Society and Section C of the American Association for the Advancement of Science, at Detroit, August 12, 1897.

2. Solubility of pentosans by digesting for two and one-half hours at three and one-half atmospheres with fifty-five cc. of water and five-tenths gram salicylic acid:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved. In per cent. of substance.	In per cent. of pentosans.
Wheat No. 1	5.80	4.54	78.27
Wheat No. 2	5.17	4.08	78.91

The pentosans which had gone into solution were determined by diluting the liquid to 250 cc. after cooling, filtering, and distilling 100 cc. of the filtrate with twelve per cent. hydrochloric acid until no furfural could be detected in the distillate. The furfural was precipitated with phenylhydrazin acetate in the usual manner.

J. König, in an article on the methods of analysis used in the examination of fodders published in *Landwirthschaftlichen Versuchs-Stationen*, **48**, 81, states that diastase also acts as a solvent for pentosans and hemicelluloses and gives the following figures:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved by diastase. In per cent. of substance.	In per cent. of pentosans.
Rye	8.90	2.22	24.95
Peas	3.62	1.02	28.17
Potatoes	2.12	0.94	44.34
Rye straw	18.07	2.74	15.22
Pea straw	10.27	1.85	18.11

If this were true, it would render the diastase method fully as unreliable as the high pressure methods and the problem of determining the exact starch content of a material would be as far from solution as ever. We therefore decided to investigate this point with the following results:

Solubility of pentosans by digesting with thirty cc. malt extract (100 grams malt to one liter of water) until all starch had been converted:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved by malt diastase. In per cent. of substance.	In per cent. of pentosans.
Wheat	5.80	0.011	0.181
Barley	6.50	0.010	0.151
Rye	8.10	0.016	0.195
		0.017	0.206
Oats	13.65	0.010	0.071
		0.010	0.071

Solubility of pentosans by digesting with five-tenths gram taka-diastase until all starch had been converted:

Substance.	Per cent. of pentosans in substance.	Pentosans dissolved. In per cent. of substance.	In per cent. of pentosans.
Wheat	5.80	0.011	0.194
		0.012	0.199
Barley	6.50	0.015	0.238
Rye	8.10	0.017	0.209
Oats	13.65	0.011	0.079

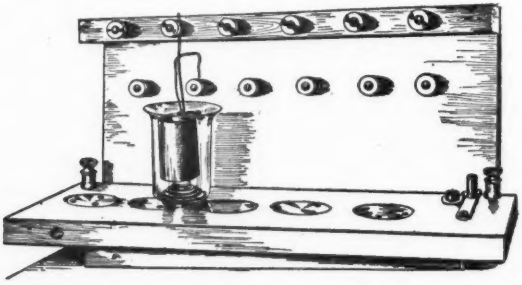
The small amounts of pentosans found here are, without doubt, not due to any solvent action of the diastase on the pentosans as it is well known that soluble starch, dextrin, sucrose, and all hexoses will yield small amounts of furfural when distilled with twelve per cent. hydrochloric acid. We are therefore justified in assuming that diastase has no solvent action on the pentosans and is a reliable means for determining the exact starch content of a cereal or fodder.

A NEW ELECTROLYTIC STAND.

By George J. Hough.

Received February 3, 1898.

THE electrolytic stand herein described was devised and made by myself, and is, as I believe, an entire novelty. It is very simple and easy of construction, and anyone with a little knowledge of tools can make it for himself.



By arranging on an upright board a double series of binding posts for the attachment of the electrodes, and also by the use of a number of copper disks in the base of the stand for direct con-

tact when platinum dishes are used as electrodes, the capacity for continuous and manifold work is great. The stand is provided with a cut-off switch to control the current, and all the wires are hermetically sealed within the stand, thus protecting them from vapors, acids, etc.

The stand, as illustrated here, consists of a base fifteen inches long, six inches wide, and about seven-eighths of an inch thick. To one of the long edges is fastened an upright piece thirteen inches long, six inches wide, and seven-eighths of an inch thick, forming the back ; and above this is the top, a piece of the same length and thickness, but only three inches wide, which projects horizontally over the back on both sides.

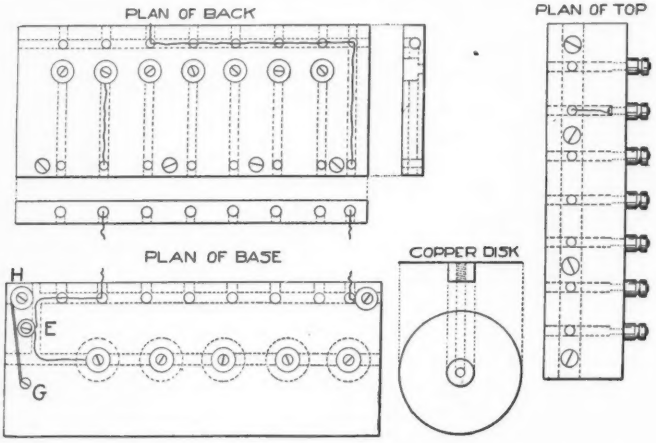
On the rear corners of the base are the two binding posts for connection with the battery wires, one of which binding posts is in connection with all the positive electrodes, and the other is in connection by means of the switch with all the negative electrodes. In the middle of the base are set the copper disks, which are of thin copper, one and three-fourths inches in diameter, and may be of any suitable number, depending on the size of the base. To one side of the copper disk is soldered a small piece of brass rod tapped with a screw thread, as is represented in the diagram. Hence it is only necessary to sink a hollow in the top of the base, so that the disk shall lie flat on the surface, and it can be readily attached in the same manner as a binding post.

At one end of the base is the cut-off switch, which is quite essential in such a stand, as it is desirable to interrupt the current while attaching or removing a solution for electrolysis. On the back of the stand at about two-thirds of its height, is a horizontal row of binding posts ; and on the front edge of the top is another row of binding posts exactly corresponding to those below them in number and position. It is well to have as many pairs of binding posts as there are disks in the base of the stand.

Small tunnels, less than one-third inch in diameter, are bored through the various parts of the stand to contain the necessary wires. The arrangement of the wires will be readily seen from the accompanying diagrams, which show the tunnels, binding posts, and copper disks, and also the small holes at the tunnel intersections for facility in wiring. In the plan of the base, G is the switch-pivot, and is in direct connection with the main bind-

ing post H, while the switch makes and breaks contact at E with the cathodes and the copper disks.

The wire used for the different connections is insulated copper wire, No. 23, though that is entirely a matter of choice, but it should not be too thick or it will be found difficult to pass it through the tunnel connections. When the wires are all in and the connections completed, all openings to the tunnels are



plugged up with paper and sealed with paraffin wax; the bases of the binding posts and disks are also filled in with wax.

The stand can easily be made in a day's work, as it only takes a short time to bore the tunnels and adjust the connections; inserting the wires is the slowest task, but when this is once well accomplished and the openings sealed up, the stand is good for a great many years' wear, as all connections are carefully protected from injury by handling or otherwise, and the only danger to guard against is the burning out of the wires by a very strong current.

In the plans given here, the binding posts on the top of the stand are intended to carry the anodes; and the binding posts on the back for the attachment of the cathodes. It will also be noticed that the copper disks are in connection as cathodes,

though of course this order can be reversed by changing the order of the battery wires at the two main binding posts.

A further accessory to the stand, not shown in the illustration, is a small pocket compass set in the base to serve as a galvanometer, to show whether or not the wires from the battery are attached to the stand in the right order. The compass is surrounded by at least two turns of wire connected with the main binding posts and controlled by a suitable switch to prevent a short circuit. It is only useful when the battery is at a distance or in another portion of the building, and the battery wires do not happen to be marked. Of course, it must be determined by experiment, in which direction the needle swings when the current is traversing the stand in the proper direction, and a little mark put on the glass of the compass to show this. I have constructed one stand with such a galvanometer. It is also well to mark the positive binding post on the base, and the set of binding posts for the anodes. This can be neatly done with a small piece of paper gummed to the board.

A stand of the size here illustrated, should not cost over five dollars, including the labor; it should be made of hard wood, and the binding posts should be "sounder posts."

A MODIFIED AIR-BATH.

By F. P. Venable.

Received January 10, 1898.

THIS air-bath is a modification of the one devised by Habermann.[1] The modifications serve to give a wider application to his bath and a publication is made of them to draw the attention of American chemists to the advantages of Habermann's idea rather than to make any claim for special originality in them.

The cut will make the construction and the use of the bath clear. A glass bell jar is provided with a knob for handling and three tubulures. One of these is for the introduction of a thermometer. The remaining tubulure on the top serves as a vent for gases and the one in the side provides for an air-current. Either or both of them may be closed with stoppers if it is so desired.

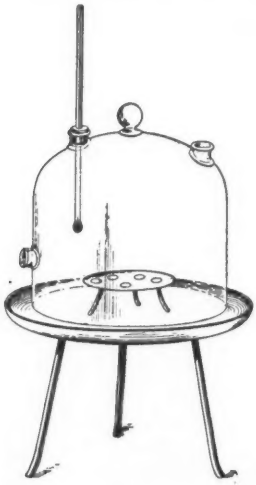
[1] *Ztschr. angew. Chem.*, 1897, 202.

This bell jar may by placed on the sand of a bath or better upon a ring of asbestos board on a sheet-iron pan or upon an iron plate. The object to be heated may be placed upon a tripod—a triangle or such a porcelain support, with perforations for crucibles, etc., as is frequently used in desiccators.

The advantages over the ordinary copper air-bath are :

1. Cheapness. A bell jar of ten inches diameter costs less than a third as much as the copper bath of the same dimensions.

2. Cleanliness. There is no corrosion from acid fumes. Incrustations upon the sides and roof of the jar are easily seen and removed so that there is no risk of their falling back into the



dishes or casseroles. It will then be especially useful for the drying down of acid solutions in the separation of silica.

3. The operation of drying can be watched.

4. The only part requiring renewal is the iron pan or plate and either one of these is very cheap. The burning out of the copper bottom of the ordinary air-bath is of distressingly frequent occurrence.

5. Any warm plate may, by this bell jar, be turned into a drying-bath in which the temperature can be watched and

regulated by increasing the thickness of the asbestos board or by other means.

I am strongly convinced of the wide application and general usefulness of this modified drying apparatus.

UNIVERSITY OF NORTH CAROLINA.

CONTRIBUTIONS TO THE CHEMISTRY OF ZIRCONIUM, NO. 8.

SOME PROPERTIES OF ZIRCONIUM DIOXIDE.

BY F. P. VENABLE AND A. W. BELDEN.

Received February 14, 1898.

THERE are so many misstatements as to the properties of zirconia in the literature of chemistry that we think it well to publish the results of our study of this body.

1. *Specific Gravity.*—The following values have been given: 4.30 (Berzelius), 4.90 (Berlin), 5.50 (Sjögren), and 5.45 (Hermann). Our determinations were made with quite pure material and yielded as a mean 5.489.

2. *Solubility.*—The strongly ignited zirconia is practically insoluble in all acids except hydrofluoric. In this it is readily soluble on heating. If soda is present along with the zirconia, as sodium zirconate, the mass is not dissolved, probably owing to the formation of sodium zirconium fluoride. The statement is frequently met with that zirconia is soluble in sulphuric acid. This is based upon observations of Berzelius and his directions are that the zirconia must be finely powdered and heated with a mixture of two parts sulphuric acid and one part water until the sulphuric acid volatilizes. Our experiments would show that it is quite insoluble in concentrated sulphuric acid and when the directions of Berzelius are followed out this dilute acid dissolves only 6.72 parts to the 1,000 parts of acid. Neither concentrated nor dilute hydrochloric acid nor nitric acid seem to have much action upon it.

Prolonged heating with sodium carbonate effects very little change in zirconia. It is only sparingly dissolved. Berzelius must have made use of a carbonate carrying some hydroxide in the experiments in which he speaks of dissolving the zirconia by means of sodium carbonate.

Again, half a gram of zirconia (finely powdered) was fused for nine hours with twenty grams of microcosmic salt.

The zirconia did not apparently enter into the fusion nor could the formation of crystals be observed as has been maintained. The same results were observed in a similar experiment with borax.

3. *Zirconium Hydroxide.*—The statement is made in Dammer's Handbook (1, 619) that of the two possible hydroxides only $ZrO(OH)_2$ is known, and that, further, numerous pyrohydrates are known whose contents of water lie between this and the anhydride. This is based upon the work of G. J. Bruch,[1] who described a meta-zirconic acid, $ZrO(OH)_2$, prepared as a white, voluminous, almost gelatinous precipitate, by precipitating a solution of a salt of zirconium with ammonia.

In the following experiments this precipitate, gotten with ammonium hydroxide, was washed free of ammonia, then placed in a Gooch crucible and washed about twelve times with alcohol (ninety-five per cent). It was then washed with ether. After weighing the crucible it was heated strongly and the loss of water was 26.50 per cent. In a second experiment the zirconium hydroxide precipitate was pressed between filter-paper, placed in a Gooch crucible, and washed with petroleum ether until there was no further loss of weight. This washing was done in an atmosphere free from carbon dioxide. Afterwards the crucible was strongly heated. The loss of water was 26.19 per cent. A third experiment carried out in a similar manner yielded also 26.30 per cent. Other experiments gave losses of 25.97 per cent. and 27.21 per cent. The percentage of water in $Zr(OH)_4$ is 22.69. It would therefore seem that treatment with petroleum ether brought the precipitate very nearly down to the composition $Zr(OH)_4$. In using alcohol and ether there seemed to be no definite limit to the removal of water and hence in several experiments final constant weights were not obtained. Two experiments gave respectively 11.11 and 9.45 per cent. of water. The percentage in $ZrO(OH)_2$ is 12.80.

A specific gravity determination of the hydroxide containing 25.97 per cent. of water gave 3.25.

4. *Solubility of the Hydroxide.*—The statement of Bruch, that this substance is soluble in 5,000 parts of water and turns litmus

[1] *Jahresber*, 1854, 729.

paper blue and turmeric paper orange-yellow is cited by several authors. This is manifestly an error. The alkaline reaction observed was doubtless due to the ammonia which it so persistently retains when ammonium hydroxide is used in the precipitation. Bailey and others have noted how prolonged the washings must be to free the hydroxide from ammonia. Experiments were carefully carried out to test this point but we failed to detect in the pure hydroxide any alkaline reaction or any appreciable solubility in pure water. Certainly it is less than the figure given by Bruch.

The solubility of the cold precipitated hydroxide in acids is as follows: It is very readily soluble in concentrated and dilute hydrochloric acid (which is the best solvent for it), in hydrofluoric acid, and in hydrobromic acid. It is very sparingly dissolved by hydriodic acid. Concentrated and dilute nitric acid dissolve it easily.

Among the organic acids it was found that oxalic acid was the best solvent, dissolving it nearly as well as the mineral acids. Saturated solutions of tartaric and citric acids dissolved less than 1 : 1,000 and glacial acetic acid also dissolved very little.

If the zirconium hydroxide is precipitated from a hot solution it is much less soluble in the dilute acids. Thus dilute hydrochloric or dilute nitric acid will dissolve only about 1 : 100 and dilute oxalic acid dissolves only about half as much. If the precipitate, however, stands for some days in contact with the acid it is dissolved to about the same extent as when precipitated cold.

As to the solubility in basic substances, ammonia (sp. gr. 0.90) does not seem to appreciably dissolve it, but when diluted (sp. gr. 0.96) there is dissolved about 1 : 10,000 parts of ammonia. Clarke[1] has shown the solubility in potassium hydroxide, and in sodium hydroxide to be as follows:

							Gram.
50	per cent.	KOH	solution	dissolved	per	cc.	0.00233
33	"	"	"	"	"	"	0.00097
25	"	"	"	"	"	"	0.00075
12	"	"	"	"	"	"	0.00009
33	"	"	NaOH	"	"	"	0.00245
25	"	"	"	"	"	"	0.0012
12	"	"	"	"	"	"	0.0005

[1] This Journal, 18, 434.

Certain salts of ammonia exert quite a solvent action. Thus a saturated ammonium carbonate solution will dissolve about 1 : 100, and a solution of ammonium tartrate rendered strongly ammoniacal has a somewhat smaller solvent action.

5. *Absorption of Carbon Dioxide.*—Zirconium hydroxide shows a decided tendency to absorb carbon dioxide. This may be observed on exposing the moist precipitate to the air or on prolonged heating at a low temperature (100°–150°) over an ordinary burner. Such a mass will gain very noticeably in weight. The extent of this absorption of carbon dioxide was tested as follows: About two grams of the moist hydroxide were placed in a porcelain boat in a tube and pure carbon dioxide passed over it for some twenty-five or thirty hours. At the end of this time the hydroxide had contracted into small, hard, horn-like particles and no further change was observable. Purified air was next passed over these particles for eighteen or twenty hours and the carbon dioxide coming off was caught in a barium hydroxide solution and determined. Then the particles were heated and the carbon dioxide was caught by a fresh solution of barium hydroxide. It was found that about one-third of the carbon dioxide which had been absorbed came off without heating. As no distinct point could be observed at which this carbon dioxide ceased coming off (no clear line of demarcation between that lost at ordinary temperatures and that lost on heating), no inferences were drawn and the carbon dioxide was all reported together. The percentages of carbon dioxide absorbed were 16.42, 5.72, and 7.05. These show a wide variation and can scarcely be taken as showing more than the fact that considerable amounts of the gas are absorbed with the formation of basic carbonates. The basic carbonate, $Zr(CO_3)_2.2Zr(OH)_4$, contains 16.68 per cent. of carbon dioxide, and $Zr(CO_3)_2.6Zr(OH)_4$ contains 7.55 per cent., and $Zr(CO_3)_2.8Zr(OH)_4$ contains 5.96 per cent.

This experiment was varied somewhat by suspending the zirconium hydroxide in water and passing carbon dioxide through the water. This gave 6.73 and 6.00 as the percentages of carbon dioxide absorbed in two separate trials.

UNIVERSITY OF NORTH CAROLINA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 27.]

AMMONIUM SELENIDE.

BY VICTOR LENHER AND EDGAR F. SMITH.

Received February 26, 1898.

BY bringing ammonia and hydrogen selenide together Bineau[1] claims to have prepared ammonium selenide. His product was a white, crystalline solid, which was readily decomposed by water in the presence of air. No mention occurs anywhere that this compound was ever obtained by crystallization from solution, hence it may be of interest to note that when prepared by the latter method it crystallizes in black, anhydrous, orthorhombic prisms. Peculiar conditions, however, seem necessary for its formation. Thus, in attempting to make ammonium selenomolybdate it was observed that when an ammoniacal solution of ammonium molybdate was saturated with hydrogen selenide gas a dark-red colored solution resulted, which yielded the black crystals of ammonium selenide upon careful evaporation. The solution contained five grams of ammonium molybdate in fifty cc. of water, to which twenty cc. of the strongest ammonia water had been added. The solution was saturated with hydrogen selenide gas. The resulting liquid, deep red in color, was concentrated in a vacuum over sulphuric acid. The final residue consisted of ammonium molybdate, metallic selenium, and well-defined, black, orthorhombic crystals. The latter were separated as completely as possible from the selenium, and extracted for several days with pure carbon disulphide. The crystalline mass, purified as far as possible in this manner, proved to be stable in the air, and dissolved readily in water to a dark-red colored solution. The latter, when freshly made, precipitated selenides from neutral or alkaline solutions of metallic salts. On exposure to the air, however, the solution of the salt suffered decomposition with the separation of black selenium. An excess of ammonia seems not to prevent the change.

The analysis gave as follows :

[1] *Ann. chim. phys.*, [2], 67, 227.

I. 0.3051 gram of substance gave 0.2137 gram selenium = 70.04 per cent. selenium.

II. 0.2031 gram of substance gave 0.1418 gram of selenium = 69.81 per cent. selenium.

Ammonium.

III. 0.2012 gram of substance gave 0.0603 gram of ammonium = 29.97 per cent. ammonium.

IV. 0.3036 gram of substance gave 0.0918 gram of ammonium = 30.24 per cent. ammonium.

The discrepancy between the found and calculated percentages is due to metallic selenium, which adhered to the ammonium selenide crystals. The salt was distilled with sodium hydroxide in determining the ammonium content. The liberated ammonia was absorbed by standard hydrochloric acid, the excess of the latter being titrated with standardized alkali.

In estimating the selenium a weighed quantity of the salt was dissolved in water containing a little sodium hydroxide. An excess of hydroxylamine[1] hydrochloride was added to this solution, from which the selenium separated completely after boiling several minutes. It was then transferred to a weighed Gooch filter, washed with water and dried at 105° for one hour. This method is far superior to the usual course of precipitating selenium by means of sulphurous acid.

The ammoniacal molybdate solution of the strength given in the preceding lines is the only solution from which the black crystals were obtained. Under these conditions the salt was always found, but with molybdate solutions of greater dilution or with such as contained arsenic acid or tungstic acid, evaporation showed nothing but metallic selenium.

UNIVERSITY OF PENNSYLVANIA.

[1] Privately communicated by Dr. H. F. Keller.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 28.]

ELECTROLYTIC DETERMINATIONS.

BY EDGAR F. SMITH AND DANIEL L. WALLACE.

Received February 26, 1898.

I. URANIUM.

SOME years ago one of us found that it was possible to completely precipitate uranium[1] from an acetate solution by means of the electric current. The deposit consisted of the hydrated protosesquioxide of uranium, which was ignited and weighed as U_3O_8. Indeed, the procedure was adopted in the separation of uranium from the alkali metals when they were associated in certain rare minerals. It has frequently been used since that time by the author and its reliability has been fully confirmed. However, Heidenreich[2] evidently experienced some difficulty in obtaining satisfactory results, for he remarks: "Versuche, Uran aus seiner Acetatlösung quantitativ abzuscheiden führten zu keinem Ergebniss, selbst bei 50-stündiger Einwirkung des elektrischen Stromes." A method, requiring fifty hours, would scarcely be regarded as having value even if the final results were really good. The following experiments, however, show that not only can satisfactory results be obtained, but they furthermore leave little doubt as to the time-factor, which is of prime importance in all determinations.

A solution of uranium acetate was prepared, which contained 0.1185 gram of urano-uranic oxide (U_3O_8) in ten cc. of the liquid To the latter volume were added five-tenths cc. of concentrated acetic acid and the whole was then diluted to forty cc. with water, when it was electrolyzed with a current N. $D_{40} = 0.18$ A. $V = 3$. The temperature of the liquid during the decomposition was 70° C. The uranium was completely precipitated in six hours. The filtrate or solution poured from the deposit showed no traces of uranium, when it was evaporated and the residue tested for that metal.

[1] *Am. Chem. J.*, 1, 329; Smith's Electrochemical Analysis, p. 94.

[2] *Ber. d. chem. Ges.*, 29, 1587.

RESULTS.

U_3O_8 present in grams.	U_3O_8 found in grams.
0.1185	0.1187
0.1185	0.1184
0.1185	0.1182

2. CADMIUM.

Those interested in electrolysis will probably remember that the writers have at various times proposed methods and conditions not only for the electrolytic determination, of this metal, but also for its separation from the more frequent associates. So often have we ourselves carried out these separations that we were inclined to believe other chemists would meet with like success. Such, however, seems not to have been the case, for in a very recent issue of this Journal[1] we felt called upon to publish very carefully outlined conditions for the complete deposition of cadmium from acetic and nitric acid solutions in order to again confirm our early statements. Heidenreich[2] mentions that the separation of cadmium from solutions containing sodium phosphate and free phosphoric acid gave results which were "ebenfalls nicht quantitativ; die letzten Reste von Kadmium sind nicht zu entfernen, selbst wenn der Strom bis 1-Ampère verstärkt wird." We regret exceedingly that this chemist has met with so little success in his efforts to repeat our work, but as in former instances of disagreement we again present new experimental evidence showing that our original suggestions were undoubtedly correct.

To ten cc. of a cadmium sulphate solution, containing 0.1656 gram of metallic cadmium, were added an excess of disodium hydrogen phosphate (1.0358 sp. gr.) and one and one-half cc. of phosphoric acid (1.347 sp. gr.). The liquid was then diluted to 100 cc., heated to 50° C., and electrolyzed with a current N. $D_{100} = 0.06$ A. Volt $= 3$. The precipitation was finished in seven hours. The metal deposits were bright and adherent. They did not show the slightest trace of sponginess. At the expiration of four hours the current was increased to N. $D_{100} = 0.35$ A. Volt $= 7$. The acid liquid was siphoned out without the interruption of the current. The pole separation, during the

[1] This Journal, 19, 870.

[2] *Ber. d. chem. Ges.*, 29, 1587.

entire precipitation, equaled one and one-fourth inches. The cadmium was washed with hot water and then carefully dried. The filtrates were examined but did not reveal a trace of unprecipitated metal. This is a direct contradiction of Heidenreich's statement that " die letzten Reste von Kadmium sind nicht zu entfernen."

RESULTS.

	Cadmium present in grams.	Cadmium found in grams.
I	0.1656	0.1654
	0.1656	0.1658
	0.1656	0.1657

UNIVERSITY OF PENNSYLVANIA.

PRELIMINARY REPORT OF THE COMMITTEE ON COAL ANALYSIS.

To the President and Members of the American Chemical Society:

At the Cleveland meeting of the American Chemical Society a Committee, consisting of W. F. Hillebrand, C. B. Dudley and W. A. Noyes, was appointed to consider the methods of proximate analysis of coal with a view to the adoption, if possible, of uniform methods for this country. After discussion among themselves, the committee have formulated the following outline of methods for analysis which they herewith submit, rather as a means of securing further information than as a final report. The committee very earnestly request all chemists interested in the matter, who may see this report, to send to the chairman of the committee a criticism of the methods proposed and a statement of any objections they see, and of any modifications which they think desirable.

Since the literature of the subject is widely scattered and much of it is not easily accessible, the committee request that all who have published papers bearing on the subject will, if possible, send to the committee reprints of such papers, or, if that cannot be done, a statement of where such papers can be found and the points covered.

Without the full and hearty cooperation of others the labors of the committee will be greatly increased and the conclusions finally arrived at will be less representative of general experience than it is desired they should be.

METHODS OF ANALYSIS.

1. *Sampling:* At least five pounds of coal should be taken for the original sample, with care to secure pieces that represent the average. These should be broken up and quartered down to obtain the smaller sample which is to be reduced to a fine powder for analysis. The quartering and grinding should be carried out as rapidly as possible, and immediately after the original sample is taken, to prevent gain or loss of moisture. The powdered coal should be kept in a tightly stoppered tube or bottle till analyzed.

2. *Moisture:* Dry one gram of the coal in an open porcelain or platinum crucible at 104°–107° for one hour, best in a double-walled bath containing pure toluene. Cool in a desiccator and weigh covered.

Question: Has any one experience with other methods of drying? over sulphuric acid, *in vacuo*, in a current of air, in watch-glasses, or otherwise? Especially in this and other cases, the committee desire any comparative results which can be furnished.

The following comparison of the effect of drying one hour in a toluene bath, twenty hours *in vacuo* over sulphuric acid, and in air over sulphuric acid was made by Dr. Hillebrand.

	One hour in toluene bath.	20 hours *in vacuo* over H_2SO_4.	In air over H_2SO_4. 2 hrs.	48 hrs.	120 hrs.
Coal No. 1.....	2.85	3.60	2.87	3.15	3.39
"	3.10	3.59	....	....	....
"	3.23	3.57	....	....	...
"	3.25	3.49	....	....	....
"	3.24	....	....	....	....
"	3.22	....	....	....	....
"	3.27	....	....	....	....
Coal No. 2.....	1.84	2.08	1.77	....	2.00
"	1.83	2.07	....	....	....
Coal No. 3.....	1.52	1.75	1.42	....	1.70
"	1.51	1.73	....	....	....
Coal No. 4.....	1.01	1.04	1.05	....	1.18
"	1.08	1.03	....	....	....
Coal No. 5.....	1.40	1.69	1.45	....	1.66
"	1.41	1.67	....	....	.. .
"	...	1.67	....	....	....
Coal No. 6.....	0.30	0.21	0.23	....	0.25
"	0.34	0.28	....	....	...

These results seem to indicate that drying *in vacuo* gives higher and, probably, more correct results than drying at 105° for one hour.

The following experiments were carried out by Mr. W. E. Burk at the Rose Polytechnic Institute[1] for the purpose of determining whether volatile matter other than water is lost in drying bituminous coals. A hard glass tube was partly filled with copper oxide, partly jacketed with a glass sleeve so that a portion could be heated to 100° by a current of steam. The coal was weighed in an aluminum boat enclosed in a weighing tube, and was then heated to 100° for an hour in a current of dry air. The moisture and any volatile matters which were expelled were passed over the heated copper oxide and the water and carbon dioxide were absorbed as usual in calcium chloride and in potash bulbs. The results were as follows:

Weight of coal taken.	Loss in weight of coal at 100°.	Water found in calcium chloride tube.	Per cent. of water in coal.	Per cent. of carbon found in potash bulbs.	Per cent. of excess of hydrogen found.
1.4217	0.1994	0.2014	14.00	0.048	0.016
1.1195	0.1596	0.1625	14.25	0.058	0.029
3.1079	0.2111	0.2113	6.78	0.022	0.001
3.2356	0.2152	0.2142	6.65	0.025	.....
2.9408	0.1967	0.1967	6.65	0.037	.....

The amount of moisture found was slightly higher than was found in the same coal by the usual method, perhaps because of the current of dry air over the coal. Since the loss of volatile matter other than water was always less then one-tenth per cent., it can safely be disregarded for most practical purposes, with coals of this class.

3. *Volatile Combustible Matter.*—Place one gram of fresh undried coal in a platinum crucible, weighing twenty to thirty grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom six to eight cm. above the top of the burner. The flame used should be twenty to twenty-five cm. high when burning free, and the determination made in a place free from draughts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. To find "Volatile Com-

[1] See Proceedings of the Indiana Academy of Sciences for 1896, p. 113.

bustible Matter," subtract the per cent. of moisture from the loss found here.

Questions: Should a larger portion be taken? Should the coal be heated more gradually at first? Should a blast be used? Can results be obtained by heating in a muffle, or in any other manner, which will agree with those obtained by this method?

The committee consider the determination as largely arbitrary, in any case, and believe that uniform results in the hands of different chemists will be best secured by making the conditions as simple as possible. The most serious objection to the method proposed appears to be the danger of mechanical loss at the commencement of the heating. It is believed, however, that the error from this source is less than would arise from any method which leaves the application of the heat to the judgment of the operator.

The committee especially desire to secure any analytical data which may be available to show the degree of concordance of results obtained by the same or different chemists. Also any comparison of analytical results with results of commercial coking.

4. *Ash.*—Burn the portion of coal used for the determination of moisture, at first over a very low flame, with the crucible open and inclined, till free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter.

Question: Are carbonates likely to be present in the ash in such amount that heating over a blast would lessen the weight appreciably?

When the sulphur in the coal is in the form of pyrites, that compound is converted almost entirely into ferric oxide in the determination of the ash and, since three atoms of oxygen replace four atoms of sulphur the weight of the ash is less than the weight of the mineral matter in the coal by five-eighths of the weight of the sulphur. While the error from this source is sometimes considerable, the committee is not now prepared to recommend such a correction.

5. *Fixed Carbon.*—This is found by subtracting the per cent. of ash from the per cent. of coke as found in paragraph 3.

6. *Sulphur.*—What methods are used? Eschka's, with sodium or potassium carbonate, fusion with sodium carbonate and potassium nitrate, Carius' or others? Any comparative results are especially desired.

7. The committee would recommend that the heating effect be calculated on the basis of the coal burned to carbon dioxide and vapor of water at 100° C., and be stated either in calories per kilogram or English heat units per pound. The theoretical evaporative effect is to be calculated by dividing the number of calories per kilogram by 536 or the number of English heat units per pound by 965. In either case it expresses the theoretical number of kilograms or pounds of water converted into steam from and at 100° C. by one kilogram or pound of the coal.

A calculation of the results of twenty-one analyses, and determinations of heating effect with the bomb calorimeter, made with Indiana and Pittsburg bituminous coals, shows that the heating effect may be found in all cases examined, with a maximum error of two per cent., by the following rule:

Subtract from 100 the per cents. of moisture and ash and one-half the per cent. of sulphur, and multiply the remainder by 80.7. The product will be the heating effect of the coal burned to vapor of water, expressed in calories.

The committee will be glad of any data which will enable them to further test this factor and also of any data with regard to other methods of determining heating effect.

Persons interested in the subject of coal analysis are requested to send any communications which they may wish to make, to Prof. W. A. Noyes, Rose Polytechnic Institute, Terre Haute, Ind.

W. A. NOYES,
C. B. DUDLEY,
W. F. HILLEBRAND,
Committee.

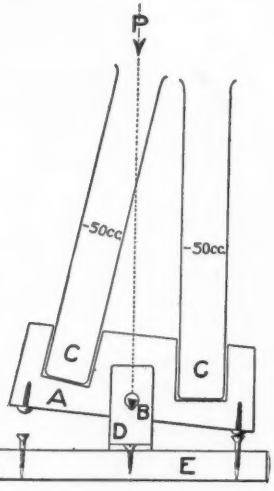
February 22, 1898.

A COLLECTOR FOR DISTILLATION OF AMMONIA FROM WATER.

By F. P. Dunnington.

Received February 4, 1898.

IN the familiar process of making a determination of free and albuminoid ammonia in water, the close attention which is demanded to change the receptacle as each of the several portions of fifty cc. is collected, is somewhat engrossing to anyone when conducting other analytical work. To avoid this embarassment I have devised the following simple apparatus, which, for lack of a better name, is called a collector.



The figure presents a section of one-fourth size. From this the arrangement and working of the apparatus may be understood. It is made as follows:

In a block of dry poplar or other light wood, A, 43 × 53 × 150 mm., a hole of three mm. diameter is made at B for the pivot, and the large holes, CC, for Nessler tubes, are placed at the

same distance from the center of the block and equally inclined, as indicated. When the Nessler tubes are twenty-nine mm. in diameter, these holes should be about thirty-one mm. and be lined with a strip of woolen cloth to afford a snug fit for the tubes. The pivot B is a knife edge, made by grinding at its ends, a piece of a double three-inch saw file about fifty-five mm. long, and is merely hammered into the small hole cut for it. The knife edge is supported by a pair of plain two-inch angle irons (such as are kept in stock at a hardware store); in each of these, the hole in the upright limb is bored out and filed to the shape shown in the figure. These irons, D, are screwed to the wooden base, E, 170×170×20 mm.

The motion of the block, A, is checked by two round-head screws fastened into the under side of A, and by two flat-head wood screws partly screwed into the block E. By screwing the latter up or down you may adjust the apparatus so that when one tube is empty and the other is being filled, as soon as the latter collects fifty cc. of water, it topples over and immediately brings the other tube under the point P, to collect the distillate. While the second tube is being filled, you may hold the block A, remove the first tube and empty or replace it by another tube of same size and weight; when the second tube has collected fifty cc. it will topple over and again bring the mouth of the empty tube under P. The screw which serves to fasten each angle iron in place also passes through one end of a slip of thin sheet brass 15×30 mm., the other end of which is bent up at right angles, so serving to keep the pivot from shifting to one side, but not binding upon it. This piece of brass is not shown in the figure, since it would cover the pivot end.

The Nessler tubes used are 29 mm. in diameter and 195 mm. long, and weigh 49 grams; should the tubes be heavier, it would be necessary to bore the hole for the pivot at a point a little higher up on the center line of the block A. It is easy to adjust this apparatus so that the amount required to topple the tubes will not vary as much as one-half cc. from the fifty cc.

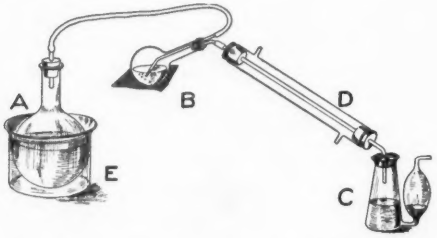
UNIVERSITY OF VIRGINIA, February 2, 1898.

BORIC ACID DETERMINATION.[1]

By Thomas S. Gladding.

Received February 7, 1898.

FOR the determination of boric acid I find the following method gives satisfactory results :



One gram of the substance in which the boric acid is to be determined is washed into flask B (150 cc. capacity), with a little ninety-five per cent. methyl alcohol. Five cc. of sirupy eighty-five per cent. phosphoric acid are added. Flask A is filled two-thirds full of ninety-five per cent. methyl alcohol and placed in the water-bath E. Flask B is now connected with the condenser D, and flask C placed in position to receive the distillate. Heat is now applied to the water-bath E and, when the methyl alcohol is boiling, flask A is connected to the tube which passes to the bottom of flask B. A current of methyl alcohol vapor is thus continually passing through the liquid in flask B, and carries over the boric acid. Heat is applied under flask B and so regulated that the liquid remains between fifteen and twenty-five cc.

The distillation is carried on in this way for about one-half hour, the distillate finally amounting to about 100 cc. A mixture of 40 cc. glycerine and 100 cc. water is now carefully neutralized, using phenolphthalein as an indicator, and then added to the distillate, which is then titrated with standard soda. The distillation must be continued until no more acid is obtained. Usually, it is complete in thirty minutes.

[1] Read before the New York Section, February 4, 1898.

A blank should be run using all the reagents, and any acidity found must be deducted from the final results.

The following results were obtained with borax and boric acid: One gram borax gave 36.57 per cent. boric acid, the theoretical per cent. being 36.65 per cent.; one gram boric acid gave 99.9 per cent. boric acid.

A distillation of crystallized boracic acid, without the addition of phosphoric or other acid, was found to yield all the boric acid present. A similar distillation of borax was found to yield 19.50 per cent. boric acid out of a total of 36.65 per cent. present, or slightly more than fifty per cent. of the whole amount. This behavior may be useful in some analyses.

A gentle suction, by means of aspiration bottle, upon flask C, is desirable to avoid loss by possible leakage.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 29.]

ACTION OF SULPHUR MONOCHLORIDE UPON MINERALS.

BY EDGAR F. SMITH.

Received March 7, 1898.

SULPHUR monochloride has frequently been applied in organic chemistry in the synthesis of various bodies, and the results obtained by the employment of this reagent have invariably had great attraction and interest for the investigator. There are, however, other directions in which the same reagent may be followed with equal interest; *e. g.*, in the action upon the natural products furnished by the mineral world. To illustrate, mention may be made of the behavior of such substances as arsenopyrite, chalcopyrite, pyrite, and marcasite with the reagent in question. Finely divided arsenopyrite and sulphur monochloride were brought together in a glass tube. After slight agitation, action set in, accompanied by the evolution of much heat, and the almost complete decomposition of the mineral. The tube was then freed from air by the introduction of carbon dioxide. It was sealed and heated to about the boiling-point of the sulphur monochloride (139°) for a period of nine hours. On cooling, beautiful olive-green colored plates or scales separated. After their removal from the tube and separation from the adherent liquid they proved to be deliquescent and

readily soluble in water. Their aqueous solution tested with potassium ferrocyanide and silver nitrate showed the presence of iron in the ferric condition, and also of chlorine. In subsequent decompositions the crystals were filtered out, and washed with petroleum ether; then they were dissolved in water and the iron content determined quantitatively by means of stannous chloride. In this manner it was proved that 32.6 per cent. of iron was present in the ferric condition in arsenopyrite. This is certainly a confirmation of the work previously carried out in this direction on arsenopyrite by Starke, Shock, and Smith.[1]

The petroleum ether solution from the ferric chloride crystals was distilled, the product diluted with water, and tested with hydrogen sulphide, when the arsenic was precipitated. Its quantity was not estimated.

Chalcopyrite treated in a similar manner with sulphur monochloride, was completely decomposed, with the production of ferric and cupric chlorides. Marcasite and pyrite also gave beautiful crystallizations of iron chloride. The decompositions were in both instances complete and the total iron content determined. On the addition of sulphur monochloride to marcasite and pyrite no action was observed in the cold. With chalcopyrite and arsenopyrite the evolution of heat, as already mentioned, was very great, so that the vessel containing them could not be held in the hand. This difference in behavior evidently indicates a marked difference in the union of the elements concerned. In pyrite and marcasite we deal with iron and sulphur alone and with them there is an absence of marked reactivity, whereas in arsenopyrite and chalcopyrite we have substitution products in which there is perhaps a less intimate union of the sulphur than exists in the pyrite and marcasite. It may be observed here that Brown,[2] while working with marcasite, found that it contained its total iron in the ferrous condition, but when this same mineral was dissolved in sulphur monochloride it gave a mass of iron chloride crystals showing the presence of about forty-one per cent. of iron in the ferric state. This would mean that this reagent undoubtedly acts as an oxidant; that its power is in a large measure due to its chlorine content,

[1] This Journal, 19, 948.

[2] *Proc. Am. Phil. Soc.*, 33, 1894.

so that we may say of sulphur monochloride, it is "chlorine in disguise." This view of its action is corroborated by other decompositions which will be presented later. The experiments upon which the preceding statements are based werecarried out by Mr. F. W. Moore.

The mineral stibnite dissolved immediately and completely in sulphur monochloride with a violent ebullition and the generation of much heat. When the solution cooled crystals separated. These were collected and heated with water, with the formation of antimony oxychloride. Much heat was also evolved when cinnabarite and sulphur monochloride were mixed. To effect complete decomposition the mixture was heated in a sealed tube. On cooling long needles were observed throughout the liquid. These proved to be mercuric chloride. Chalcocite was also completely decomposed, with the production of a crystalline powder, which on examination was found to be cupric chloride. This is additional evidence of the oxidizing character of the solvent employed, and explains the reason for the obtainment of so much ferric chloride when using marcasite, which contains its iron in the ferrous condition. Tetrahedrite, although of a complex nature, yields in the cold to the influence of the sulphur monochloride, and crystals of ferric chloride appeared in a very short time, although to effect the complete decomposition of the mineral it was necessary to heat it with the reagent to 140° C. Sphalerite was not attacked in the cold, and at 150° its decomposition was very slight, but at 250° C. complete solution occurred. On cooling, a mass of anhydrous zinc chloride separated. This was quickly collected and treated with water when it dissolved with a hissing noise. The zinc in solution equaled 67.5 per cent.

Galenite, furthermore, was not affected in the cold, but at 250° C. was changed completely to lead chloride. Finely divided molybdenite was not attacked in the cold, nor was it entirely broken up after heating to 300° C. Many of these experiments show that, where the sulphur estimation of a sulphide is not desired, this method of decomposing such minerals may be of use in analysis. This is particularly true in the case of tetrahedrite. Mr. C. S. Reeve was kind enough to conduct these experiments for me.

At my suggestion, Mr. E. W. Pierce brought pure, artificial arsenic trisulphide in contact with sulphur monochloride. A violent reaction set in, and much heat was liberated. On repeating the experiment at a temperature of 0°, the reaction took place slowly with the gradual solution of the metallic sulphide and the appearance of a slight residue of sulphur, which disappeared on the addition of more sulphur monochloride. Nothing separated when the liquid was further chilled. Arsenic sulphide was precipitated from the diluted solution on the addition of hydrogen sulphide. The minerals linnæite $(Co,Ni)_3S_4$, millerite (NiS), gersdorffite (NiAsS), and rammelsbergite $(NiAs)_2$, were also fully decomposed by the monochloride on heating the mixture in sealed tubes to 170° C. Metallic chlorides were formed in all instances and separated from the cold solutions. Cobaltite (CoAs), smaltite $(Co(FeNi)As_2)$, and ullmannite (NiSbS), in a finely divided condition, were dissolved by the sulphur monochloride when heated to 180° C. in a sealed tube. These observations were made by Mr. Jos. Cauffman, who also found that rutile in powdered form was decomposed almost completely by the same reagent, with the production of titanium tetrachloride. This behavior suggested heating the oxides of molybdenum, tungsten, tantalum, and columbium, as well as the minerals wolframite, scheelite, and columbite with the same reagent, when all were dissolved, and from the cold solutions beautiful crystalline bodies separated. Some of these have been analyzed, while others are yet under examination and will be discussed in a later communication. The indications are that the action of the sulphur monochloride in these substances is both oxidizing and substituting. Combinations of the metallic haloids with sulphur monochloride are not produced. In the case of the sulphides and sulpho salts which were investigated, quantitative determinations of the products were only made in a few instances, for there was no question as to the completeness of the decompositions, and the character of the resulting bodies. Upon considering the facts which are here presented, we recognize that with the sulphides of non-metals, for example stibnite, the action is violent, and the decomposition complete. This is also true of arsenopyrite where arsenic probably facilitates the transposition, whereas with marcasite, pyrite, sphalerite, galenite,

etc., the reaction is more sluggish. From an examination of the excess of sulphur monochloride in these different experiments it would seem that the original sulphur of the mineral is merely dissolved out, for upon evaporation it separates in large quantities.

UNIVERSITY OF PENNSYLVANIA.

THE DETERMINATION OF SMALL QUANTITIES OF ALCOHOL.

BY FRANCIS G. BENEDICT AND R. S. NORRIS.

Received March 12, 1898.

THE methods for the determination of alcohol ordinarily in use are for the most part physical. By means of the pycnometer, vaporimeter, and ebullioscope, we are able to determine with reasonable accuracy the amount of alcohol present in alcoholic beverages and solutions, which seldom contain under one per cent. of ethyl alcohol. When, however, the exact estimation of smaller quantities is desired, these methods are unsatisfactory.

The numerous chemical methods for the determination of alcohol depend for the most part on the oxidizing action of potassium bichromate, chromic acid, or potassium permanganate. Only a small portion of the research on the oxidizing action of these compounds, has been done with reference to their oxidation of alcohol. This is partly explained by the previous existence of the physical methods of analysis above referred to and by the fact that while many organic compounds are completely and readily oxidized to carbon dioxide and water, alcohol is oxidized with great difficulty, the oxidation ceasing usually with the formation of acetic acid. The iodoform reaction and the blue coloration produced with a sulphuric acid solution of molybdic acid, furnish tests of the greatest delicacy, and for the most part investigators have been satisfied with a qualitative demonstration of the presence of alcohol when occurring in such small quantities as to preclude the use of the ordinary quantitative methods.

Bodländer[1], pursuing an investigation similar to that for which the methods here reported were devised, *i. e.*, the estimation of

[1] *Pflüger's Archiv*, 32, 398.

the small quantities of alcohol eliminated in the urine and breath of man, used a standard solution of chromic acid in concentrated sulphuric acid and estimated the alcohol by determining the amount necessary to completely reduce a given volume of this solution. He states that the oxidation of alcohol is complete; *i. e.*, the products are carbon dioxide and water. Bourcart[1], Heidenhain[2], Freyer[3], and Kuriloff[4] find on the other hand that the oxidation with chromic acid or potassium bichromate ceases with the formation of acetic acid. Rose[5] used potassium permanganate as the oxidizing agent, and states that the alcohol was completely oxidized to carbon dioxide and water by decinormal potassium permanganate in a solution that contained forty per cent. of sulphuric acid.

Bodländer's method was tried and found not to give entirely satisfactory results owing to the formation and escape of aldehyde, the amount formed varying with slight changes in the manipulation. On the addition of a dilute solution of alcohol to the concentrated sulphuric acid solution of chromic acid, the odor of aldehyde can be easily detected. Furthermore the end-point is rather difficult to determine.

Potassium permanganate, in the presence of strong sulphuric acid, was tried as an oxidizing agent. It was necessary to heat the solution in order to complete the oxidation, and under these conditions the potassium permanganate is decomposed in the absence of reducing agents. It is believed however, where only approximate results are required, that the conditions can be determined under which the oxidation is complete, while the decomposition of the potassium permanganate, other than that produced by the alcohol, is very slight. The method used was to mix a definite volume of decinormal permanganate with forty per cent. of its volume of concentrated sulphuric acid, in a glass-stoppered flask. To this mixture the solution of alcohol was added from a burette, in small quantities at a time, and thoroughly mixed with it by shaking. The excess of permanganate was then determined by titration against a standard solution of

[1] *Chem. Centrbl.*, *1890*, **1**, 547.
[2] *Ztschr. anal. Chem.*, *1893*, **32**, 360.
[3] *Chem. Ztg.*, **19**, 1184; *Ztschr. anal. Chem.*, *1897*, **36**, 328.
[4] *Ber. d. chem. Ges.*, **30**, 741.
[5] *Chem. Centrbl.*, *1888*, 308.

ferrous ammonium sulphate. For certain purposes in the investigation it was necessary to determine the alcohol vapor contained in a current of air, and since it was found that the permanganate solution was reduced by simply passing the air of the room through it, this reagent could not be used.

As we were not successful in securing the accuracy desired with any of the methods tried, it became necessary to devise one which would give fairly close results for solutions containing as low as 0.01 per cent. of ethyl alcohol.

The method adopted depends on the oxidation of the alcohol by an excess of chromic acid in a concentrated sulphuric acid solution, and the determination of the excess of chromic acid by titration against ferrous ammonium sulphate solution, the end-point being established by a few drops of standard permanganate solution. The reagents required for the determination are :

1. A solution of chromic acid in concentrated sulphuric acid.
2. A solution of ferrous ammonium sulphate.
3. An approximately decinormal solution of potassium permanganate.
4. A standard solution of alcohol in concentrated sulphuric acid.
5. Chemically pure, concentrated sulphuric acid.

The chromic acid solution is made by dissolving 2.2064 grams of chemically pure potassium bichromate in just enough distilled water to effect complete solution, and then making up to 500 cc. with concentrated sulphuric acid, care being taken not to let the temperature rise to over 100° C. This corresponds to a solution containing three grams of chromic anhydride in one liter. The reagent preserved in a glass-stoppered bottle is fairly stable.

For the ferrous ammonium sulphate (Mohr's salt) solution forty grams of the pure salt are dissolved in water and, after the addition of thirty cc. of concentrated sulphuric acid, the solution made up to a liter. Made in this way the solution is very stable, showing but slight changes on comparatively long standing.

The potassium permanganate solution is made by dissolving three and three-tenths grams of the crystallized salt in a liter of water.

The standard alcohol solution is practically a solution of ethyl

sulphuric acid in concentrated sulphuric acid. About two grams of five per cent. alcohol (see below) are weighed into a fifty cc. graduated flask and concentrated sulphuric acid added slowly, keeping the mixture cool to prevent any volatilization of alcohol by immersion in cold water. After five cc. of the acid have been added in this way the flask is filled to the fifty cc. mark and the solution mixed by pouring back and forth into a beaker.

The alcohol used in preparing the standard was one of the better grades of commercial alcohol. Its strength was determined with the admirable pycnometer described by Dr. Squibb.[1] This pycnometer readily gives the specific gravity of alcohol to the fifth or sixth decimal place. Ostwald's pycnometer,[2] which has the advantage of being much cheaper, was also found to give quite satisfactory results.

An accurate table for determining the per cent. of alcohol in solutions containing forty per cent. of absolute alcohol or over, from the specific gravity, is given by Dr. Squibb in his *Ephemeris*.[3] For solutions containing less than forty per cent. the table[4] used by the Association of Official Agricultural Chemists is to be recommended.

A practical difficulty arises in weighing out small quantities of strong alcohol owing to its volatility. It is therefore recommended that an approximately five per cent. solution be first made, from which small quantities can be correctly weighed without material loss. For preparing this solution the following method was found to be the most satisfactory: A glass-stoppered Shuster dropping bottle such as is ordinarily used to contain indicators, was weighed when dry and clean. After adding about the required quantity of alcohol its weight was again taken. The alcohol was poured into a previously tared flask, the last traces being removed by careful washing with distilled water. The solution was then made up to the desired weight, and the per cent. of absolute alcohol in it calculated.

It is of the utmost importance that the concentrated sulphuric

1 This Journal, **19**, 3.

2 Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen, W. Ostwald, p. 110.

3 *Ephemeris*, **2**, 541.

4 Bulletin No. 46, Division of Chemistry, U. S. Department of Agriculture, p. 65.

acid used in these experiments be free from organic or other reducing matter.

To find the value of each solution in terms of the other, the ferrous ammonium sulphate is first titrated against the potassium permanganate. A measured volume of the chromic acid solution, generally ten or twenty cc., is then poured into 100–200 cc. of water, enough of the ferrous ammonium sulphate solution added to completely reduce it, and the excess of ferrous ammonium sulphate determined with the potassium permanganate. Twenty cc. of a chromic acid solution of the above strength oxidizes about seventeen cc. of the ferrous ammonium sulphate solution. Owing to the viscosity of the chromic acid solution it is necessary to adopt a definite method of delivery in order to obtain the same quantity each time. This result was secured by allowing the solution to run freely from an ordinary pipette made to deliver ten cc. Toward the end of the delivery the drops ceased quite suddenly to fall in quick succession and followed each other only at intervals of several seconds. The first "slow" drop was taken and the pipette removed immediately. This method apparently gave equal volumes of liquid.

The amount of chromic acid required to oxidize a given weight of alcohol, was determined by means of the standard solution of alcohol in concentrated sulphuric acid. Ten cc. of chromic acid solution were drawn off into a small flask, and a measured amount (about three cc.) of the standard solution of alcohol added from a burette.[1] The mixture was heated with constant agitation over a free flame to 98° C.[2] (a thermometer being held in the solution) and kept at about this temperature for five minutes. Under these conditions no aldehyde was formed. After cooling the solution it was poured into 200 cc. of water, ferrous ammonium sulphate added from a burette until the red color of the chromic acid had entirely disappeared, and the excess of ferrous ammonium sulphate titrated back with the potassium permanganate.

[1] Considerable time is required for the sulphuric acid solution to run down the sides of the burette. The readings should not, therefore, be made until it is ascertained that the meniscus is stationary.

[2] According to Cross and Bevan, *J. Chem. Soc.*, **53**, 889, chromic acid in concentrated sulphuric acid solution gives off oxygen at 105° C. Numerous tests showed no decomposition of the chromic acid solution after five minutes' heating at 98° C.

The standard solution of alcohol used contained 237.6 mgms. of alcohol in 100 cc. In four titrations of this solution we obtained the following results:

	Alcohol solution.	Equivalent in ferrous ammonium sulphate solution.	Ferrous ammonium sulphate solution equivalent to one cc. of alcohol solution.
	cc.	cc.	cc.
I.	4.00	9.70	2.43
II.	4.95	12.00	2.42
III.	2.95	7.20	2.44
IV.	3.10	7.60	2.45
Average			2.43

Since a cubic centimeter of the alcohol solution contained 2.376 mgms. of alcohol, one cc. of the ferrous ammonium sulphate solution would be equivalent to 0.978 mgms. of alcohol. This factor was used in calculating the alcohol in the other solutions.

In order to test the accuracy of the determination, solutions of different strengths were made by the method used in preparing the standard solution.

The following results were obtained upon analysis:

	Weight of alcohol.		Volume of solution.	Per cent. of alcohol.	
	Calculated. Mgms.	Found. Mgms.	cc.	Calculated. Per cent.	Found. Per cent.
I.	38.18	38.18	100	0.038	0.038
II.	30.63	30.05	50	0.071	0.070
III.	853.00	885.00	500	0.171	0.177
IV.	7.24	7.12	100	0.00724	0.00712
V.	11.01	11.23	50	0.02202	0.02246

An extremely dilute solution was made by diluting 12.34 mgms. of alcohol to 250 cc. The solution therefore contained 0.00494 per cent. of alcohol. The result obtained by titration was 0.00508 per cent., an error of about one ten-thousandth of one per cent. of alcohol.

In order to compare the accuracy of the method with that of Squibb's pycnometer for dilute solutions of alcohol, 31.44 grams of 90.61 per cent. alcohol was made up to 994.5 grams with water, giving a 2.865 per cent. solution. With Squibb's pycnometer the result was 2.95 per cent. when calculated from a table in the *Ephemeris*[1] and 2.84 per cent. when calculated from a more recent table.[2] By titration with the chromic acid the

[1] *Ephemeris*, **2**, 563.

[2] Bulletin No. 46, Division of Chemistry, U. S. Department of Agriculture, 65.

strength was determined to be two and eight-tenths per cent.

As previously stated, one of the conditions to which the method must apply, was the determination of small quantities of alcohol in an air current.

Concentrated sulphuric acid according to our experiments removes alcohol from an air current even more completely than it does water. The apparatus with which this great affinity of sulphuric acid for alcohol was determined, consisted of a system arranged as follows: A current of air drawn by means of an ordinary Chapman filter-pump passed successively through a U-tube filled with cotton, a gas-washing cylinder containing concentrated sulphuric acid, a U-tube filled with soda-lime, a U-tube containing a known amount of alcohol, a cylinder similar to the first containing concentrated sulphuric acid, a 12-inch piece of combustion tubing containing a layer of copper oxide kept at a red heat by a four-tube burner, and a U-tube containing glass beads covered with about ten cc. of barium hydroxide solution, which in turn was connected by a rubber tube to the filter-pump. The tube with cotton was used to remove dust from the air. The sulphuric acid in the first cylinder removed the water, and the soda-lime the carbon dioxide. The air then passed over the alcohol and carried some of it into the sulphuric acid in the second cylinder. In case any of the alcohol was not absorbed by the sulphuric acid it would be burned by the hot copper oxide to form carbon dioxide, which would produce a precipitate in the barium hydroxide solution. Air was passed through the apparatus at the rate of 600 cc.[1] a minute.

In an experiment in which about nine-tenths gram of nineteen per cent. alcohol evaporated in nine hours, no barium carbonate was formed. In two other experiments in which half that quantity of alcohol was used it was also completely absorbed by the

[1] That it is possible to remove the alcohol quite completely from a current of air passing at a much more rapid rate than this, was subsequently demonstrated with a slightly modified apparatus. Owing to the fact that a rapid air current caused the combustion of the rubber stopper in the end of the short tube containing the copper oxide, by the hot air drawn against it, a tube thirty inches long was used and heated only at one end. The barium hydroxide U-tube in the apparatus above described, also was not very satisfactory for rapid currents of air, and was therefore replaced by a gas-washing cylinder containing about twenty cc. of barium hydroxide solution. A current of air containing alcohol vapor drawn through this apparatus at the rate of 2100 cc. a minute, produced only a slight turbidity in the barium hydroxide solution in the course of fifteen minutes. When the cylinder containing sulphuric acid was removed from the system, however, a heavy precipitate was instantly formed.

sulphuric acid. Forty cc. of concentrated sulphuric acid were used in each case.

Four solutions were prepared by this method and the alcohol determined by titration. The results obtained were as follows:

	Alcohol absorbed. Mgms.	Alcohol determined. Mgms.
I.	96.77	95.05
II.	90.87	89.66
III.	41.62	41.50
IV.	13.5	14.4

Two experiments were made to determine how much alcohol a given volume of concentrated sulphuric acid can completely remove from a current of air. In the U-tube immediately preceding the acid ninety per cent. alcohol was placed and its evaporation was facilitated by a loose roll of filter-paper in the limb of the tube next to the acid. Air was drawn through this apparatus for fifteen hours at the usual rate before a distinct appearance of barium carbonate precipitate occurred. The coating of the carbonate on the sides of the barium hydroxide tube was, at the end of this period, less in amount than that produced by the combustion of a milligram of alcohol. During the period approximately forty cc. of alcohol was evaporated. The sulphuric acid solution measured about ninety cc. and had a brownish-red color and a faint, pleasant, ethereal odor. It was made up to 100 cc. with concentrated sulphuric acid and five-tenths cc. measured out and made up to fifty cc. with more acid. This solution was titrated with the chromic acid solution and found to contain 3.43 mgms. of alcohol in each cubic centimeter. Accordingly the fifty cc. of concentrated sulphuric acid used in the first experiment had absorbed 34.3 grams of alcohol.

In the second experiment only thirty cc. of sulphuric acid were used, and the alcohol was made to evaporate more rapidly. About twenty cc. of ninety per cent. alcohol were volatilized in eight hours. In the beginning of the experiment the rapid absorption of the alcohol by the sulphuric acid caused an appreciable rise in the temperature. The sulphuric acid solution was diluted as in the first experiment, and the alcohol determined to be 1.72 mgms. in each cubic centimeter. The thirty cc. of sulphuric acid had therefore absorbed 17.2 grams of alcohol.

For the determinations of alcohol in dilute solutions we have found the following method the most satisfactory. Having prepared the standard solutions above described and determined the value of each in terms of the others, the strength of the unknown solution of alcohol is first determined roughly by means of an ordinary pycnometer.

If the solution contains more than one per cent. of alcohol. weigh out accurately such a quantity as will contain about one-tenth gram of absolute alcohol into a fifty cc. graduated flask and add ten cc. concentrated sulphuric acid carefully, the flask being immersed in cold water and continuously shaken to prevent a rise in temperature. The solution is then made up to the fifty-cc. mark with concentrated sulphuric acid, thoroughly mixed, transferred to a burette and about five cc. drawn off into a small flask. Twenty cc. of the chromic acid solution are then added, using the same precautions for the delivery of the solution as when it was standardized. The contents of the flask are heated to 98° C (a thermometer being immersed in the liquid) and kept at this temperature for five minutes. The solution is then cooled down to the room temperature, poured into 200 cc. of distilled water and ferrous ammonium sulphate added from a burette until the excess of chromic acid is completely reduced, as is indicated by the disappearance of the red color. The excess of ferrous ammonium sulphate is then determined with the standard potassium permanganate. It is best to add a single drop of the potassium permanganate solution at first in order to be sure that there is an excess of ferrous ammonium sulphate present. The amount of alcohol per cubic centimeter is calculated thus: The amount of ferrous ammonium sulphate solution used (after making allowance for the permanganate required for the back titration) is subtracted from the number of cubic centimeters of ferrous ammonium sulphate equivalent to the chromic acid solution used, and the result divided by the number of cubic centimeters of the alcohol solution taken. This gives the volume of ferrous ammonium sulphate solution in cubic centimeters equivalent in reducing power to one cc. of the solution of alcohol. Multiplying this by the factor previously determined, which expresses the number of milligrams of alcohol equivalent to one cc. of ferrous ammo-

nium sulphate, gives the weight of alcohol in one cc. of the sulphuric acid solution.

If the original solution contains one per cent. or less of alcohol, draw 0.5 cc. into a 100-cc. flask and add about five cc. of concentrated sulphuric acid, keeping the liquid cool during the addition. Add ten cc. of the chromic acid solution and proceed as above. This determination will serve to indicate approximately how much alcohol there is in the solution so that in subsequent titrations enough of it can be taken to reduce from sixty to eighty per cent. of the chromic acid. The amount of sulphuric acid added in each case should be equal to about twice the volume of the solution of alcohol used.

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ALUMINUM USED AS AN ELECTRODE.

BY GEORGE J. HOUGH.

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AS the result of a number of experiments in quantitative chemical analysis by electrolysis, I take pleasure in stating that aluminum can be used as a substitute for platinum, as an electrode, though only to a limited extent.

It can be used as the cathode with nitric acid solutions, and apparently is not affected by the electrolytic action. Theoretically, it should not be affected as a cathode during the electrolysis, any more than the metals are affected which are precipitated there.

It is unserviceable, however, as an anode, as it is readily oxidized at that pole and dissolved in the acid solution. Neither can it be used in sulphate or chloride solutions, as the free acid readily attacks it; but if the sulphate or chloride solution be changed to the double oxalate of potassium or ammonium, as recommended by Classen, the aluminum cathode is not affected. This aluminum cathode can also be used with cyanide solutions, for although aluminum is readily attacked by hot solutions of potassium cyanide or oxalate, it apparently is not affected in the cold, even under electrolytic action.

The idea of substituting aluminum for platinum as an electrode, was suggested to me by the fact that aluminum is not

affected by hot or cold nitric acid, and metals plated on it could be readily dissolved off without injuring the electrode; but as the best aluminum on the market is not quite pure, there is a possibility in time of a slight loss in weight. Even with this drawback, however, aluminum cathodes will be serviceable for ordinary commercial analysis, especially copper analysis, in which I think they would find their greatest field of usefulness.

It has been suggested to me that aluminum, heavily plated with platinum, might be made to serve as an anode; but of this I am somewhat doubtful, as I have not yet had opportunity to try it.

This substitution of aluminum for platinum I make simply as a suggestion, for my experiments have not been numerous enough or minute enough to announce it as a scientific improvement, except in the case of copper analysis.

But should it prove to be sufficiently adapted to the purpose which I have designated, it has two great advantages: first, as compared with platinum it is very much lighter, and its use would reduce the liability to error in the weight of the deposited metal, which is small as compared with the weight of the electrode; second, it is vastly cheaper than platinum, costing only one-sixtieth as much in the manufactured condition.

NOTE ON LIQUID PHOSPHORUS.

By F. P. VENABLE AND A. W. BELDEN.

Received February 14, 1898.

IN 1875 Hourton and Thompson[1] reported the formation of a peculiar modification of phosphorus formed on boiling ordinary phosphorus for five minutes with a strong solution of potash. The alkaline solution was poured off and the liquid phosphorus washed. It is said to remain liquid for months and solidifies only on cooling to $+3.3^{\circ}$. It is further reported as not oxidizing in the air nor giving off light in the dark. On becoming solid it forms ordinary wax-like phosphorus and a second variety of crystalline phosphorus.

These singular statements are cited in Dammer's "Handbuch dèr anorganischen Chemie" and the chemical literature available to us has been searched in vain for any further mention of this

[1] *Arch. d. Pharm.*, (3), 6, 49.

strange variety of phosphorus. It has therefore seemed advisable to give a brief notice of some experiments in which it was attempted to form this liquid phosphorus.

Five grams of fresh wax phosphorus were placed in a flask with 80 cc. of a saturated solution of potassium hydroxide and boiled for five minutes in a neutral atmosphere (nitrogen was used). This was washed with water at 19° and on the second washing the phosphorus solidified. If the alkaline solution was poured off directly, the phosphorus caught fire, hence it was usually poured off to small bulk, diluted with water, and again poured off and so on until the phosphorus was washed. In every experiment performed the phosphorus solidified after the second or third washing. The amount of phosphorus, the time of boiling (three, five, ten, and fifteen minutes), and the strength of the potassium hydroxide solution (saturated to ten per cent. solution), were each varied without securing the liquid phosphorus.

It is, however, true that the phosphorus becomes liquid on heating under the alkaline solution and, if left covered with the same, stays liquid a long time, solidifying only when strongly cooled. It seems to give off occasional bubbles of gas during this standing and is probably being slowly changed into phosphine at ordinary temperatures. We are quite at a loss to know how the authors mentioned above secured their liquid phosphorus and how it could prove unalterable in the air. In all of our experiments it was peculiarly inflammable.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNITED STATES DEPARTMENT OF AGRICULTURE, NO. 32.]

CALORIES OF COMBUSTION IN OXYGEN OF CEREALS AND CEREAL PRODUCTS, CALCULATED FROM ANALYTICAL DATA.[1]

BY H. W. WILEY AND W. D. BIGELOW.

Received March 10, 1898.

PRINCIPLES INVOLVED.

THE calculation of the heat of combustion of food products is now quite generally practiced in analytical determinations. The development of the methods of burning in com-

[1] Read before the American Chemical Society and Section C of the American Association for the Advancement of Science, at Detroit, August 12, 1897.

pressed oxygen as proposed by Berthelot and Veille, has made it possible to use this process for ordinary purposes, and with a fair degree of accuracy. The data obtained by combustion in oxygen become, therefore, a check upon ordinary analytical determinations, as well as an additional means of measuring the dietetic value of foods. When the data obtained on combustion are to be used in analytical methods it is necessary to compare them directly with the data calculated from chemical analysis. A large number of difficulties arises in connection with this calculation on account of the number of combustible substances present in the cereals and their products. We have three great classes of bodies in cereals, namely, carbohydrates, proteids, and oils. In addition to these, however, there are many others which are oxidizable, and which yield heat in the process, among them amid compounds of nitrogen, organic acids, lecithins, and coloring-matters. These last named, it is true, exist in minute quantities, but the combustion of the whole of them is attended with a considerable evolution of heat, which must not be lost sight of in exact comparisons. In addition to this, the groups of like matters which form the chief part of cereals and cereal products are composed of several substances. In the carbohydrates are found many different classes whose heats of combustion vary largely. For instance, there is a wide difference between the heat of combustion of a gram of pentosans and a gram of starch, and midway between these lies the number representing the heat of combustion of sucrose. The different vegetable oils vary greatly in their calorific power, and these differences must be taken into consideration in the calculations. In respect of the heats of combustion of the vegetable proteids, but little is known, and we have not yet isolated sufficient quantities of the different proteids to determine the heat of combustion of each one directly. This part of the subject will be investigated further. The results of the actual determinations, however, show that the average number of small calories per gram of vegetable proteids evolved in burning in oxygen is not far from 5900.

CALORIES OF THE CARBOHYDRATES.

The details of the processes employed for cereals and cereal

products will be considered by classes, beginning with the carbohydrate group.

The magnitude of the calorimetric equivalents of the carbohydrates and their derivatives shows in general regular and expected variations, depending on their constitution and molecular configuration. Isomeric bodies show similar but not always identical heats of combustion. For the three groups of carbohydrates, presented by the formulas $C_6H_{12}O_6$, $C_{12}H_{22}O_{11}$, and $(C_6H_{10}O_5)_n$ respectively, the heats of combustion at constant volume for one gram-molecule are about 673, 1351, and 678 calories respectively. In derivatives of the carbohydrates the heat value decreases in general with the increase of the hydrogen and oxygen atoms with reference to the carbon atoms, but this rule is not rigidly applicable, and does not permit a sure judgment in respect of heat value based on a knowledge of chemical composition alone. The heat value of the pentoses is generally less than that of the hexoses, and of the hexoses the more condensed forms, as for instance the disaccharids and polysaccharids, like starch, have a higher heat value than the simpler forms like dextrose. In round numbers the heat value of the pentoses (arabinose, xylose) and of lactose (crystallized), dextrose and fructose, is 3750; of sucrose, maltose, and lactose (anhydrous) 3950; and of starch and cellulose 4200 calories per gram. In computing the heat value of a mixed carbohydrate body from analytical data, it is therefore necessary to know approximately the relative quantities of these typical constituents. If, for instance, in a cereal (ground wheat) containing seventy-four per cent. of carbohydrates it is desired to calculate the heat value accurately, it is first necessary to distribute the total carbohydrates into groups. Suppose it be found on analysis that the total carbohydrates are composed of the following quantities:

	Per cent.
Pentosans	4.5
Cellulose (soluble and insoluble fiber)	4.5
Sugar (sucrose)	1.0
Starch	64.0

The heat value of the pentosans is about fifty calories greater than for the pentoses, and the factor for pentosans is therefore $3750 + 50 = 3800$. Cellulose and starch have practically the

same heat value, and the factor for these in round numbers is 4200. The sugar is chiefly sucrose, and the factor for this is 3950. The above numbers give the necessary data for the computation given below.

COMPUTED CARBOHYDRATE CALORIES FOR ONE GRAM OF A CEREAL FLOUR CONTAINING 74 PER CENT. OF CARBOHYDRATES.

	Gram.
Total weight of carbohydrates	0.740
Weight of pentosans, etc	0.045
Weight of starch, cellulose, etc	0.685
Weight of sucrose, etc	0.010

Then:

	calories.
0.045 × 3800 =	171.0
0.685 × 4200 =	2877.0
0.010 × 3950 =	39.5
Sum	3087.5

CALORIES OF COMBUSTION OF VEGETABLE PROTEIN.

In respect of the heat of combustion of the vegetable proteid matters, it may be said that even greater variations are noticed than with the glycerids and carbohydrates; for instance, the calories obtained by the combustion of a gram of gluten, as ascertained by Berthelot, are represented by the number 5990.3. The mean number of calories per gram of the proteids in general is stated by Stohmann to be 5730.8. The calorimetric numbers for hordein, edestin, leucosin, zein, myosin, vitelin, gliadin, glutenin, and the other minor proteid bodies occurring in the cereals, have not been determined. Moreover, it must be remembered that the cereals contain a certain proportion of amid nitrogenous bodies, the heat values of which are considerably less than those of the pure proteids. It is a question, therefore, of considerable difficulty to select a factor which represents the proper number for computing its fuel value from the total nitrogen present in a cereal. In the "Principles and Practice of Agricultural Analysis", III, 559, the factor 5500 calories per gram is proposed as a suitable one for use with the proteids. This factor is probably too low for estimating the heat produced by the combustion of cereal protein in oxygen. Before the proteids are absorbed into the body and oxidized or distributed as con-

stituents of the tissues they are converted in the digestive organs into soluble forms, to which the general term peptones has been applied. The heat of combustion of peptones is decidedly less than that of the ordinary proteids, being represented by a factor 5300 calories per gram. The number given above, therefore, *viz.*, 5500 calories per gram, is about a mean to be used in calculating the calories of combustion of peptones and proteids. For the actual calculation of heats of combustion in oxygen of proteid matter of cereals to be compared with the heats of combustion obtained in the calorimeter, the factor 5900 is proposed as the one most nearly correct, in so far as our present knowledge is concerned.

We have made efforts to secure sufficient quantities of the pure proteids present in the different cereals to determine directly their calorific power. Owing to the difficulty of preparing these proteids in the large quantities sufficient for the work we have not yet succeeded in our object. We will, however, continue this work and either obtain the samples from others or, if unable to do this, prepare them ourselves, in order that the special factor for each cereal may be determined experimentally. In the absence of these special determinations we have only the recourse of making use of the factor which seems to be nearest the proper one for all; namely, 5900 calories for each gram of vegetable protein present in the cereal.

If all the nitrogen in a cereal product be calculated as proteid matter, the factor to be used in calculating the calories of combustion must be less than 5900. The reason for this is that a small part of the nitrogen present is in a non-proteid form, existing as compounds distinctly less calorifacient than protein matters. Only an approximate factor can be proposed for this calculation. It is best to determine the non-proteid nitrogen and then use the factor 5900 for the residual proteids. The nitrogen as amids in this case, in so far as its fuel value is concerned, is to be calculated by a different factor. Asparagin may be selected as a representative vegetable amid, and the calories corresponding to one gram of asparagin are represented by the number 3400. Asparagin contains 22.7 per cent. of nitrogen, and in order to convert amid nitrogen to asparagin its percentage is multiplied by 4.05. These data afford the basis of a

rational computation of heat values of the nitrogenous constituents of cereals.

Example.—The sample of wheat flour before mentioned contains 2.00 per cent. of nitrogen, of which 0.12 per cent. is of an amid nature. The proteids in the sample are calculated as follows:

$$1.88 \times 5.70 = 10.71 \text{ per cent.}$$

The amid bodies, as asparagin, are found from the following equation:

$$0.12 \times 4.05 = 0.48 \text{ per cent.}$$

In one gram of substance the calories of combustion are calculated as follows:

	calories.
0.1071 gram proteids × 5900 =	631.9
0.0048 " asparagin × 3400 =	16.3
Total calories due to nitrogen compounds,	648.2

CALORIES OF COMBUSTION OF CEREAL OILS.

In order to secure a basis for rational work, the oils of the cereals were extracted and purified as carefully as possible by the usual methods. Three of these oils have already been subjected to combustion, while the process of the purification of the others is still going on. The oils which have been burned gave the following calories per gram: Wheat oil, 9359; rye oil, 9322; Indian corn oil, 9280. For the nearest round numbers the factor for wheat oil would be 9350, and for rye and Indian corn 9300.

In making calculations from analytical data, however, the ether extract does not represent a pure oil, but all the other bodies in the cereal which are soluble in ether. It is therefore deemed desirable to determine the calorifacient power of the ether extract, obtained according to the methods of the official agricultural chemists. For this purpose a considerable quantity of the ether extract of wheat, oats, barley, and rye was prepared, and the combustion of this extract was made directly. The results per gram of ether extract for the several cereals mentioned are as follows· Wheat, 9070; oats, 8927; barley, 9070; and rye, 9196 calories. The nearest round numbers for these bodies would therefore be wheat, 9100; oats, 8950; barley, 9100; and rye, 9200.

In the extraction of cereals with ether it should not be forgotten that a portion of the fatty matter is not brought into solution. Especially is this true of the lecithins. In view of this fact, it is a matter of question whether it might not be advisable, with the present light on the subject, to multiply the ether extract by the round number 9300 rather than by the number corresponding to the calorifacient power of the ether extract itself as given above. With the exception of oats and Indian corn, the difference between the two factors would be very slight, because the ether extract is a small number. With oats and Indian corn, however, the difference would amount to several calories. In the case of oils in general, the calories of combustion vary greatly with the character of the glycerids. It has been shown, for instance, that a gram of oleomargarin when burned in oxygen affords about 200 more calories than a gram of butter-fat. The natural oils which exist in plants vary in respect of their calorific values. Linseed oil, for instance, has a slightly higher calorific value than olive oil. In Volume III of "Principles and Practice of Agricultural Analysis," p. 569, it is recommended to use the factor 9300 as an approximately correct expression of the heat value of a gram of glycerids. This is probably not far from the correct number for the average of animal and vegetable glycerids, being possibly a little too low. Since in natural cereals we have to do only with vegetable glycerids, and in breads often with a mixture of vegetable and animal glycerids, it is difficult to determine in every case the magnitude of the factor to be employed. For the pure cereal glycerids, however, it is recommended that the factor mentioned above be used; *viz.*, 9300 calories per gram. In the baking of bread, the fats, especially those in the crust, are subjected to a high temperature, under which they possibly undergo a preliminary oxidation. In this case, therefore, the factor given in the "Principles and Practice of Agricultural Analysis," *viz.*, 9300 calories per gram, may be too high.

In the ether extract of cereals there are other bodies besides fat, and it would not be proper to regard the whole mass as having the same fuel value as pure fat. It is difficult to make any accurate allowance for these bodies, which are, moreover, of an organic nature, and capable of yielding considerable quantities

of heat on combustion. To avoid confusion it may be said that the factor 9300 calories per gram may be used also with the ether extracts of flours and meals as well as with those of the baked products. In the sample of ground wheat already mentioned the ether extract is 2.00 per cent. The calories afforded by the oil in burning one gram of flour are therefore

$$0.020 \text{ gram} \times 9300 = 186 \text{ calories.}$$

It is evident that it is impracticable to make any account in our calculations of the heat of combustion arising from the oxidation of the small quantities of coloring-matters, organic acids, and other bodies not included in the above data. By using the factor 9300 for the multiplication of the ether extract instead of the factors determined by direct investigation it is evident that a sufficient allowance will be made for the inclusion not only of the bodies mentioned, but also of the lecithins remaining unextracted, and for which the calorifacient value approximates that of the true glycerids. The above data then give the basis for calculating the entire calorific power of a whole wheat flour having the following composition :

		Per cent.
Carbohydrates	Starch, cellulose, etc., 68.5 Pentoses 4.5 Sucrose 1.0	74.00
Proteids		10.71
Amids		0.48
Oil		2.00
Ash		2.00
Moisture		10.81
		calories.
Calories due to	starch, cellulose, etc	2877
" " "	pentosans	171
" " "	sucrose	40
" " "	proteids	632
" " "	amids	16
" " "	oil	186
Total calories in one gram		3922

COMPARISON OF CALCULATED AND ASCERTAINED CALORIES.

The principles of calculation which have been developed above have been applied in the direct comparison of the calories of combustion ascertained by experiment and those calculated

from analytical data. The samples of cereals examined consisted of two samples of wheat, one of rye, one of unhulled oats, and one of hulled barley. The analytical data obtained by careful analyses follow :

CHEMICAL COMPOSITION OF SAMPLES OF GRAIN.

	Wheat No. 1. Per cent.	Wheat No. 2. Per cent.	Rye. Per cent.	Unhulled Oats. Per cent.	Hulled Barley. Per cent.
Moisture	11.33	10.65	11.71	9.26	12.20
Ash	1.69	1.77	2.31	3.78	0.93
Ether extract	2.00	2.24	1.63	4.72	0.92
Protein	12.19	14.44	11.69	9.63	10.44
Sucrose	0.33	0.48	0.42	0.17	0.18
Invert sugar	0.027	0.08	0.068	0.031	0.017
Galactin and dextrin	0.160	0.25	0.220	0.260	0.140
Pentosan	5.80	5.17	8.10	13.65	6.50
Fiber	2.15	2.56	2.36	12.81	0.80
Starch	64.51	62.69	61.78	45.98	68.03

The calculated calories for each of the samples given above are as follows :

CALORIES IN SAMPLES OF GRAIN.

Component parts.	Wheat No. 1. Per cent.	Wheat No. 2. Per cent.	Rye. Per cent.	Unhulled Oats. Per cent.	Hulled Barley. Per cent.
Ether extract	186	208	152	439	86
Proteids	719	852	690	568	616
Pentosans	220	196	308	519	247
Sucrose	13	19	17	7	7
Starch and fiber	2800	2741	2694	2469	2891
Totals	3938	4016	3861	4002	3847

The calories found by direct combustion in oxygen were as follows :

Wheat No. 1	3,922
Wheat No. 2	4,011
Rye	3,909
Oats	4,181
Barley	3,886

The direct comparison of the two numbers is seen in the following table :

COMPARISON.

Variety of grain.	Calculated. calories.	Found. calories.	Difference. calories.
Wheat No. 1	3,938	3,922	+16
Wheat No. 2	4,016	4,011	+ 5
Rye	3,860	3,909	—49
Oats	4,002	4,181	—179
Barley	3,846	3,886	—40

In the above data all the nitrogen has been computed as protein.

The agreement between the calculated calories and those actually determined in the bomb is satisfactory in the above cases with the exception of the sample of oats. In this case, as will be seen, the calories directly ascertained were 179 greater than those calculated from the analytical data. This fact suggests the possibility of the heat of combustion of the unseparated complex representing the unidentified carbohydrates of hulls and fodders being higher than for starch. Where such a difference exists the suggestion at once occurs that either the analytical data or the calories obtained by combustion are in error. One of the principal values of ascertaining the calories of combustion in analytical work is indicated by such a difference. The combustion will be a check on the analysis, and vice versa the analysis a check on the combustion. Where the differences are as great as noted, the indications are for a repetition of both the analysis and the combustion. The magnitude of the difference between the calculated and ascertained calories which can be allowed as fully within the ordinary errors of analysis and combustion can only be fixed by a long series of determinations, and perhaps after the factors employed for the calculations have been slightly changed to harmonize more closely with ascertained results. At the present time, we are inclined to the opinion that when the difference between the calculated calories and those ascertained on combustion does not exceed fifty to seventy-five calories, the check is sufficiently satisfactory.

We have applied the above process to the investigation of some of the cereal products; *viz.*, flour, bread, breakfast and partially prepared foods and some miscellaneous products. The data which are given below include all of the determinations made on the products mentioned with the exception of six,

where the difference between the ascertained and calculated calories was so great as to indicate an error in one or the other.

The following table contains all the data showing a comparison between the calculated and ascertained calorific power of the several substances mentioned:

COMPARISON OF CEREAL PRODUCTS.

Name of substance.	Determined calories per gram.	Calculated calories per gram. N×5.70.	N×6.25.
Flapjack flour	3700	3776	3790
Pancake flour	3820	3833	3845
Griddle-cake flour	3724	3706	2719
Patent flour	3870	3880	3894
Mean	3779	3779	3812
BREAD.			
Vienna	4420	4372	4394
Vienna	4381	4339	4359
Home-made	4558	4483	4503
Home-made	4436	4450	4465
Mean	4449	4411	4430
BREAKFAST AND PARTIALLY PREPARED FOODS.—WHEAT PRODUCTS.			
Shredded whole wheat biscuit	4253	4298	4314
Wheat germ meal	4362	4404	4420
Gluten butter wafers	4610	4605	4628
Whole wheat gluten	4544	4542	4566
Cooked gluten	4432	4406	4425
Germea	4445	4403	4417
Breakfast gem	4379	4405	4420
Cracked wheat	4453	4395	4413
Mean	4435	4432	4450
MISCELLANEOUS.			
Kaffee-brod	4146	4203	
Granula	4385	4399	
Imperial granum	4485	4462	
F. F. V. malt food	4470	4465	
Granulated barley	4365	4353	
H-O oatmeal	4800	4799	
Mean	4442	4447	

A study of the above data reveals the fact that while the variations in individual instances are considerable, a comparison

of the means shows that the factors which have been adopted must be very nearly correct, inasmuch as the mean calculated calories differ very little from those determined by actual combustion. In calculating the calories for wheat products both the factors 5.70 and 6.25, for converting nitrogen into proteid matter, have been used. Inasmuch as the calorific power of the protein is slightly greater than that of the carbohydrates, the total calories as calculated by the factor 6.25 are slightly greater than those calculated by the factor 5.70. In the case of breads and other baked products the differences are not so great as we had anticipated, on account of the difficulty of completely extracting the fat and oil from a bread. The individual differences, as in the case of a flour, are somewhat marked, but the means agree very closely.

While this paper was writing, in point of fact on August 2, we received Bulletin 35 of the Wyoming Station (June 1897) in which Prof. Slosson has called attention to work similar to ours which he has done at that station. The factors used by Prof. Slosson differ slightly from those which we have adopted, his factor for fat and oil being 9500, for protein 5700, and for carbohydrates 4200. In nineteen samples of wheat products the calculated calories from analytical data by our factors are 4472, and by Slosson's factors 4447. In six samples of miscellaneous cereal products, calculated by our factors, the number is 4833, and by his, 4810.

It is seen by the above that the mean results are not very greatly different from the two sets of factors, Slosson gaining in his higher factor for fat a portion of what he loses in his lower factor for protein as compared with our numbers.

In conclusion we beg to call attention to the fact that in the light of the data which have been presented in the above paper, we can with reason claim that the determination of the calorific power by combustion under pressure in oxygen is destined to be a valuable aid to the analyst in serving as a check upon the analytical data. We are further warranted in believing that whenever the calculated calories and the analytical data in hulled cereals and cereal products differ by as much as 100 from those obtained by combustion, the chemist will do well to repeat both the analysis and the combustion in order to discover the source

of error. The bomb calorimeter in this way becomes a valuable adjunct to the chemist in his work from a purely analytical point of view.

The data of heat determinations in bodies rich in cellulo-lignolignin matters such as bran, hay, straw, and fibers generally, are found to be regularly higher than when calculated from the data of analysis, and this leads us to the belief that these bodies exist in a state of greater molecular condensation than starch. If this be the case, the determination of the heat of combustion may prove helpful in approximately fixing the molecular weight of the polymers in any series insoluble in reagents without change. This subject we are now investigating, and it will form the theme of a subsequent communication.

PRELIMINARY NOTE ON SOME NEW DERIVATIVES OF VANILLIN.

By A. E. Menke and W. B. Bentley.

Received March 5, 1898.

WHEN chlorine is allowed to act for some time on a solution of vanillin in chloroform, a white crystalline substance is formed, which after suitable purification and analysis was found to be chlorvanillin, melting-point 166°.

If chlorvanillin in small quantities be treated with sodium amalgam, chlorvanilloin can be obtained, melting-point 255°. We have not yet succeeded in obtaining chlorvanillin alcohol. Fusion of chlorvanillin with caustic potash seems to yield chlorprotocatechuic acid, melting-point about 235°.

The action of dilute nitric acid in suitable proportion upon vanillin yields three products: a white substance containing nitrogen, almost insoluble in the usual solvents, melting-point about 300°; a yellow compound soluble in hot alcohol, almost insoluble in water, melting-point 178°–179°; and dinitroguiacol, melting-point 123°, soluble in water. The substance melting at 178° is either nitrovanillin or an addition compound of nitrovanillin and dinitroguiacol. By treatment with nitric acid it yields dinitroguiacol, and by oxidation with permanganate forms nitrovanillic acid, melting-point 214°.

In an attempt to prepare chlorprotocatechuic acid, directly from protocatechuic acid, we found that passing chlorine in excess

through an alcoholic solution of protocatechuic acid we obtained a resinous matter, which yielded, upon treatment with caustic potash, a substance that could be precipitated by water. This body crystallizes well from alcohol in white crystals, melting-point about 178°. Analysis showed it to be tetrachlorpyrocatechin. By varying the strength of the solution of protocatechuic acid, we obtained a different product. The fuller study of these compounds is in progress, and the complete results will be published in a later paper.

ARKANSAS INDUSTRIAL UNIVERSITY.

NEW BOOKS.

INTRODUCTION TO ELECTROCHEMICAL EXPERIMENTS. BY DR. FELIX OETTEL, translated (with the author's sanction) by EDGAR F. SMITH. Philadelphia: P. Blakiston, Son & Co. 1897. 144 pp. Price 75 cents.

THE FREEZING-POINT, BOILING-POINT, AND CONDUCTIVITY METHODS. BY HARRY C. JONES. Easton, Pa.: The Chemical Publishing Co. 1897. vii + 64 pp. Price 75 cents.

The great development of physical chemistry in the last few years is calling into existence a considerable literature upon the subject, and it is a happy fact that much of this literature is of the nature of monographs. In this way each author writes from his own experience rather than by compilation, and his writing is correspondingly valuable. Such is the character of the two brief works before us.

Dr. Oettel's book is best described by the opening sentence of the translator's preface: "The purpose of this little volume is to furnish technical chemists and all persons interested in the applications of electricity in chemical manufacture with a concise guide, containing in a compact form all that is essential for the comprehension and solution of problems arising in this comparatively new field of chemical investigation." Its usefulness is wider however, for it lays down principles which are at the basis of electrochemistry not only in technology, but also in analysis and in research work in pure chemistry. The first sixty pages are devoted to the source, measurement, and regulation of the current; then follow the arrangement of experiments, with reference to vessels, diaphragms, electrodes, etc.; phenomena observed in electrolysis, including decomposition pressure, cur-

rent efficiency, transference of ions, etc.; preliminary experiments; calculation of necessary power; and lastly about forty pages of "practical part" including as a practical problem the working of an arsenical copper liquor. The book will be useful in every laboratory where any electrochemical work is done. It is almost needless to add that a translation by Dr. Smith is well done.

Dr. Jones' book, as indicated by its title, is confined to those three physical-chemical methods which find most frequent application in the laboratory. The descriptions of the freezing-point and the boiling-point methods are each preceded by a brief historical sketch and a theoretical discussion of the method, including the processes of calculation. Under the application of the freezing-point method to the determination of molecular weights, the apparatus of Beckmann and its manipulation is carefully described, and in its application to the measurement of electrolytic dissociation, the method of work with the author's apparatus is given. Similarly under the boiling-point method the apparatus of Beckmann, Hite, and that of the author are described, and a detailed account of the method of carrying out a determination follows. Under the conductivity method, the theory is also first discussed and then its application to the measurement of electrolytic dissociation. This book thus brings together in brief space the essentials of theory and practice of these three methods, and is a valuable guide to students in laboratories of physical chemistry.

Both books are of excellent typography, have very complete tables of contents, and neither has an index.

JAS. LEWIS HOWE.

PRACTICAL EXERCISES IN ELECTROCHEMISTRY. By DR. FELIX OETTEL. Translated by EDGAR F. SMITH, Professor of Chemistry in the University of Pennsylvania. Twenty illustrations. Philadelphia: P. Blakiston, Son & Co. 1897. vii + 92 pp. Cloth. Price 75 cents.

Electrochemistry is becoming year by year of more importance and assistance to the analyst and manufacturer, and any work, historical or descriptive, that adds to our knowledge of the subject is to be commended. The book in question is no more than its name indicates, but it is all that it indicates, for the exercises and examples given are not only practical and simple, but are

most clearly and lucidly set forth. As the translator says in his preface, "The examples given are not only simple, but they are also types of definite processes." Starting with suggestions as to current sources and general apparatus, there follow chapters on the testing and calibration of measuring apparatus, the influence of current density, concentration, temperature, etc., upon the fall of bath-pressure in the electrolyte, influence of current density and concentration on the course of reactions, application of gas analysis to electrochemical reactions, experiments with a diaphragm, metal precipitations with soluble and insoluble anodes, experiments with molten electrolytes, and with multipolar electrodes. The last chapter on organic electrolysis is by Prof. Dr. K. Elbs. The book should be used by all teachers and students in this field and Dr. Smith is to be thanked for giving us this excellent translation.

W. WALLEY DAVIS, JR.

LABORATORY EXPERIMENTS ON THE CLASS REACTIONS AND IDENTIFICATION OF ORGANIC SUBSTANCES. By ARTHUR A. NOYES, PH.D., and SAMUEL P. MULLIKEN, PH.D. Easton, Pa.: The Chemical Publishing Co. 1897. 8 vo. 28 pp. Price 50 cents.

The authors have collected and thrown into the form of a series of laboratory experiments the various characteristic reactions for different classes of carbon compounds. Workers in organic chemistry gradually acquire a familiarity with these reactions, but the authors have performed a distinct service to the teachers of organic chemistry in bringing them together, where the beginning student can find them, and in emphasizing their importance from an analytical standpoint. This little book might be called the beginning of a qualitative analysis for the carbon compounds, a field which is not yet far advanced.

From this point of view the writer is inclined to regret that the authors did not extend their work beyond the limit of its present twenty-eight pages and make it a more complete collection of the reactions that can be used for the identification of different classes of organic bodies, and supply it with an index so that it would be of use to more advanced workers as well as to the beginners in organic synthesis. The book should find a place in every organic laboratory. G. M. RICHARDSON.

BOOKS RECEIVED.

Irrigation Experiments in Sugar Beet Culture. By Elton Fulmer. Bulletin 31. Washington State Agricultural College, Experiment Station, Pullman, Wash. December, 1897. 30 pp., with a map of Irrigation district.

The Feeding Value of Salt Marsh Hay. By J. B. Lindsey and B. K. Jones. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass., January, 1898. 48 pp.

A Digest of Metabolism Experiments, in which the balance of income and outgo was determined. By W. O. Atwater and C. F. Langworthy. Bulletin No. 45. Office of Experiment Stations, U. S. Department of Agriculture, Washington, D. C. 1897. 434 pp.

The Calorific Power of Fuels. By Herman Poole, F.C.S., New York: John Wiley & Sons. 1898. xv + 255 pp. Price $3.00.

Quantitative Chemical Analysis by Electrolysis. By Dr. Alexander Classen, in cooperation with Dr. Walter Löb. Authorized translation by William Hale Herrick and Bertram B. Boltwood. New York: John Wiley & Sons. 1898. xii + 301 pp. Price $3.00.

Bulletin No. 10. 1. The Wooly Mullein. 2. The Gape Discase of Poultry. 14 pp. 4 half-tone plates. Bulletin No. 71. 1. Official Analysis of Commercial Fertilizers. 2. Analyses of Other Samples. 10 pp. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky. 1897.